Residue Analysis of Organic Pollutants in Sediments from the Amman/Zarqa Area in Jordan

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Dissertation

von

Mufeed Issa Batarseh

aus Jordanien

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By

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to my wife…….Maysa,

to my daughter…….Zain,

and to my……parents, sisters and brothers.

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Abbreviations

ACE	Acenaphtene
ACY	Acenaphtylene
AD3	After site D3 (20 m)
AG	Analytical grade
ANT	Anthracene
AR	Analytical reagent
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]flouranthene
BD3	Before site D3 (20 m)
BghiP	Benzo[g,h,i]perylene
BkF	Benzo[k]flouranthene
BOD_5	Biological oxygen demand
CBz	Chlorinated benzenes
CHC	Chlorinated hydrocarbons compounds
CHR	Chrysene
CH	Cyclohexane
COD	Chemical oxygen demand
^oC	Degree Celsius
D	Wadi Dhuleil tributary
d	Day
DahA	Dibenzo[a,h]anthracene
<DL	Below detection limit
DL	Detection limit
DO	Dissolved oxygen
d.w.	Dry weight
EA	Ethyl acetate
ECD	Electron capture detector
eV	Electron volt
FD3	Far from site D3 (700-800 m)
FLA	Fluoranthene
FID	Flame ionization detector
FLE	Fluorene
GC	Gas chromatography
GC/MS	Gas chromatography coupled with mass spectrometry
GPC	Gel permeation chromatography
H	n-Hexane
HCBz	Hexachlorobenzene

HCH	Hexachlorocyclohexane
HOC	Hydrophobic organic compounds
JIWS	Jordanian Industrial Wastewater Standards
IcdP	Indeno[1,2,3,4,c,d]pyrene
IDL	Instrument detection limit
I.site	Industrial site
ISTD	Internal standard
KTR	King Talal Reservoir
LOD	Limit of determination
MeOH	Methanol
MS	Mass spectrometry
N	Normality
NA	Not analyzed
ND	Not detected
NAP	Naphthalene
OCP	Organochlorine pesticides
PAH	Polyaromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCBz	Pentachlorobenzene
PHE	Phenanthrene
PYR	Pyrene
R	Zarqa River
R^2	Correlation coefficient
Ref.site	Reference site
RSD	Relative standard deviation
S	Summer season
SD	Standard deviation
ΣHCH	Sum of α-,β-, γ and δ-hexachlorocyclohexane
ΣPAH	Sum of 16 PAH compounds
ΣPCB	Sum of 6 PCB congeners
SU	Scale Unit
TBAS	Tetrabutylammoniumsulfate
TDS	Total dissolved solids
TOC	Total organic carbon
Total-P	Total phosphorous
TSS	Total suspended solids
US EPA	United States Environmental Protection Agency
v/v	Volume to volume ratio
W	Winter season

WAJ	Water Authority of Jordan
WSPs	Wastewater stabilization ponds
WWTP	Wastewater treatment plant
Z	Seil Zarqa tributary

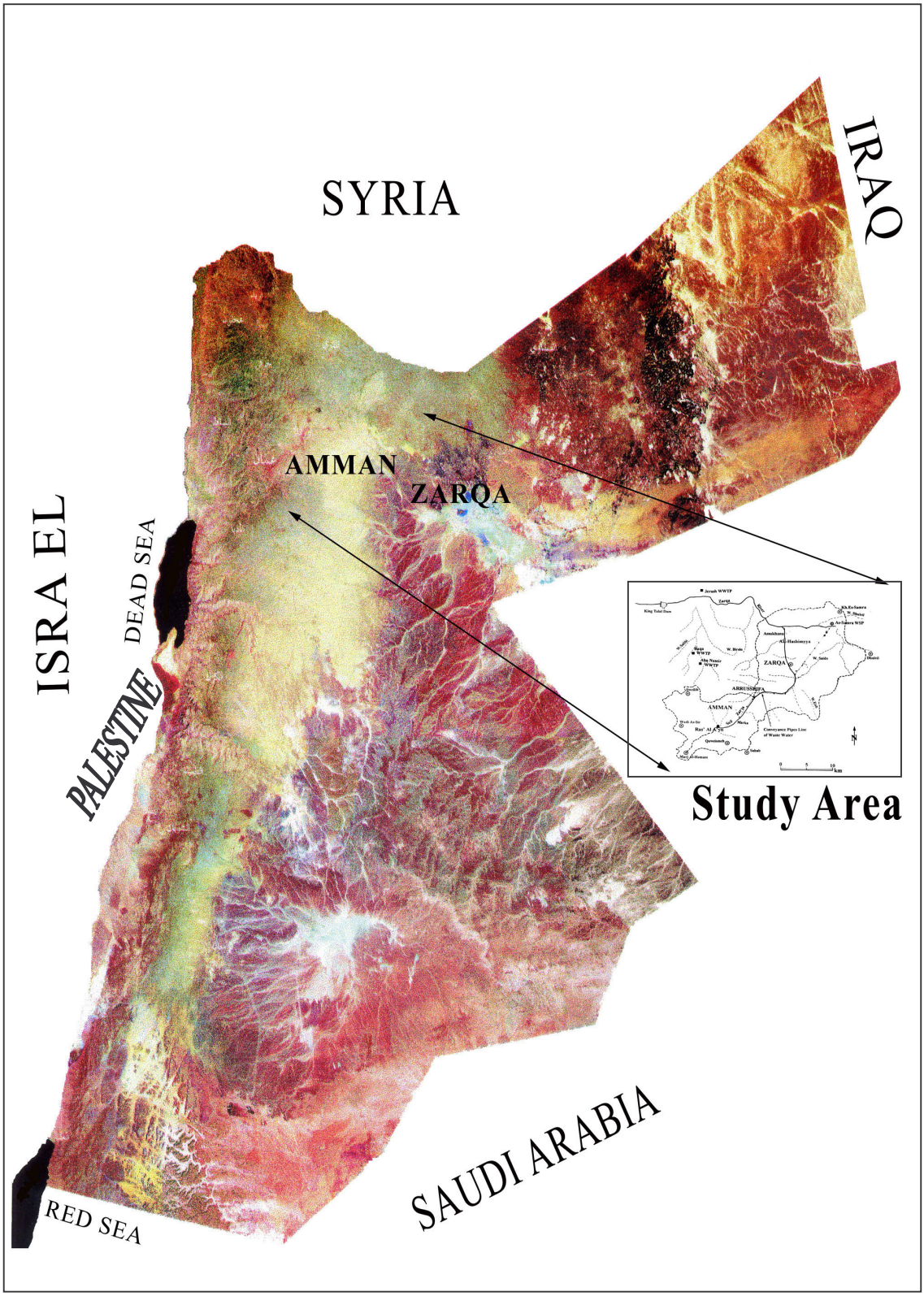


Figure 1.1. Satellite photo for Jordan shows the political borders and the location of the study area.

1. Introduction

The environment is a dynamic system and could be disturbed by human activities. It is a matter of global concern to safe the environment, “we are living and sharing one planet and one environment”. In these context the environment can be demonstrated by the five environmental media, namely atmosphere, hydrosphere, geosphere, biosphere, and anthrosphere (Manahan, 1999). These environmental media are interchanging the materials and interacting each other through several pathways. The anthrosphere which can be defined as a part of the environment made by humans and used for their different activities and the derived terminology “anthropogenic activities” is widely used to address most sources of chemical pollution introduced into the environment. For instance, each year there are large quantities of chemicals synthesized or produced which found their ways to the different environmental compartments: soil, water, and air. The task of the environmental chemists is to study the behavior, accumulation and degradation of the chemical pollutants. Therefore, environmental analysis and monitoring studies are playing a major role to evaluate the environmental quality and to obtain information about a given environmental situation. The application categories of environmental analysis and monitoring studies are summarized in **figure 1.2**. However, the present work can be classified under measurement of pollutants concentration category, in order to evaluate the environmental quality and to measure the environmental background concentrations.

Hydrophobic organic compounds (HOC) which are of global interest on account of their toxicity and ubiquity, are characterized by low volatility, low water solubility, and long-term persistence in the environment. For example, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), organochlorine pesticides (OCP), and chlorinated benzenes (CBz) are all HOC and can be potentially found in all environmental compartments including air, water, soil, sediment, and biota. The physical and chemical properties are accounting their behavior in the environment. The sediments are forming a sink in aquatic systems to adsorb a wide range of organic pollutants. The distribution of hydrophobic organic compounds between water and sediment has been found to be linearly related to the organic content in both phases, also correlated to the clay fraction in sediments (Kukkonen and Landrum, 1996).

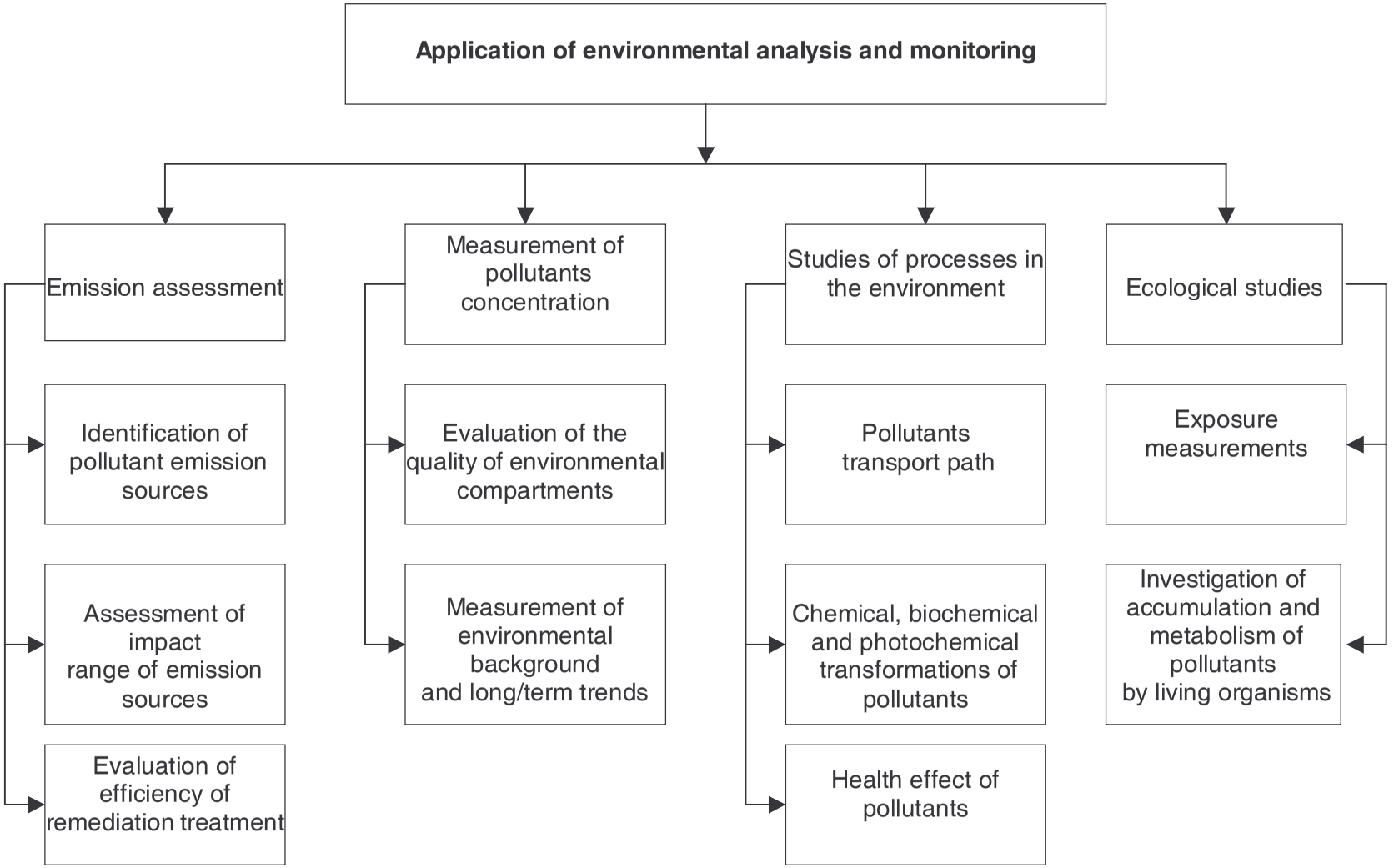


Figure 1.2. Application areas of environmental analysis and monitoring (Namiesnik and Zyqmunt, 2002).

The principle of the adsorption process of natural organic matter and xenobiotics on the sediment particle is presented in **figure 1.3**. The sediment particle can be viewed as an inorganic base that contains one or more minerals and is coated with the natural organic matter. The natural organic matter consists mainly of macromolecules of humic and fulvic acids, which are playing an important role in partitioning of hydrophobic compounds between water and organic matter phases. A conceptual model for PAH-sorption in hydrophobic region of organic macromolecules is presented in **figure 1.4**.

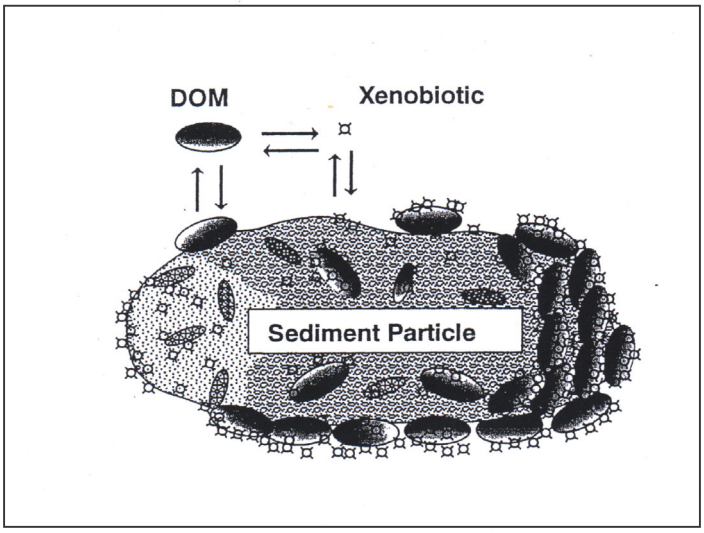


Figure 1.3. Model of sediment particle and adsorption process. The dissolved organic matter (DOM) forms a coating on the inorganic base particle with the subsequent binding of a xenobiotic mainly to the organic matter (Kukkonen and Landrum, 1996).

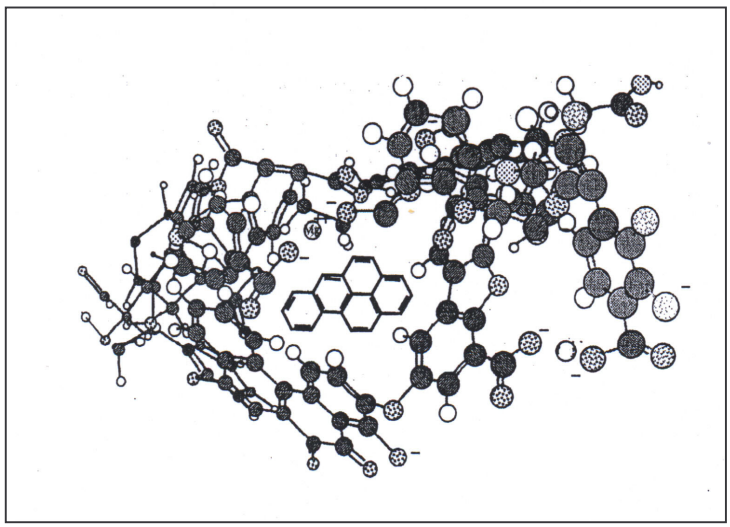


Figure 1.4. Conceptual model for the xenobiotic-sorption in hydrophobic regions of the organic macromolecules, exemplified for benzo[a]pyrene (Engebretson and Wandruszka, 1994).

The compounds investigated are discussed below in more details. Firstly, the United States Environmental Protection Agency (US-EPA) has defined 16 polynuclear aromatic hydrocarbons (PAH) as priority pollutants. Their occurrence, behavior, and distribution in the different environmental compartments have been the hot subject of continued research (Meneie et al., 1992; Miles and Delfino, 1999; Jiries et al., 2000; Lazzari et al., 2000; Krein et al., 2000). PAH are tend to accumulate in sediments and found to be linearly correlated to the total organic carbon (Kolb et al., 1995; Kukkonen, 1996). They are formed and released into the environment through natural and anthropogenic sources. The natural sources include volcanic activities and forest fires, whereas, anthropogenic sources come from incomplete combustion processes of fossil fuel and coal, incineration processes, domestic and industrial waste disposals (Pérez et al., 2001). The European Union has been limited the total PAH content in sewage sludge to be used for agriculture by 6.0 mg/kg (European Commission, 2000), however, no regulations limited the contamination levels of PAH in sediments.

Secondly, polychlorinated biphenyls (PCB) are man-made chemicals and synthesized by substituting variable number of chlorine atoms (from 1 to 10 chlorine atoms) onto the biphenyl aromatic molecular structure to produce 209 congeners. **Figure 1.5** represents the general formula of PCB. These congeners were manufactured and processed primarily for use as insulating fluids and coolants in electrical equipment and machinery in USA from 1929-1977, with a peak production in the year 1970 about 100,000 tons (Spiro and Stigliani, 1996; US-EPA, 1979). PCB have caused birth defects and cancer in laboratory animals, and they are a suspected cause of cancer and adverse skin and liver effects in humans. EPA estimates that 150 million pounds of PCB are dispersed throughout the environment, including air and water supplies; an additional 290 million pounds are located in landfills in USA (US-EPA, 2000). Polychlorinated biphenyls are characterized by high chemical, thermal, and biological stability. In addition they have low vapor pressure, low water solubility, and high dielectric constants. These congeners were used widely as coolant in power transformers, insulators in capacitors, heat transfer fluids, fire resistance, plasticizers as well as in consumer products such as ink, paper and paints. Due to their wide range of application, high environmental persistence and high bioaccumulation potentials, they are expected to spread and accumulate in different environmental compartments. The industrial waste disposal could be the main source of the PCB in the environment. Environmentally prevalent concentrations of PCB congeners were detected in different

environmental compartments worldwide (Kaiser et al., 1985; Ristola et al., 1996; Fernández et al., 1999; Xu et al., 2000; Strandberg et al., 2000; Jeong et al., 2001).

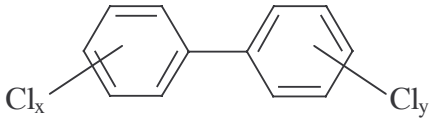


Figure 1.5. General formula of PCB, X and Y are number of chlorine atoms, where X = 1-5 and y = 0-5.

Thirdly, pesticides are products applied to control insects (insecticides), nematodes (nematicides), rodents (rodenticides), fungi (fungicides), and weeds (herbicides). Pesticides are an area of global concern for maintaining and protection environmental quality. They are used by a wide spectrum of users, from individuals, to companies, municipalities etc. Pesticides could enter the aquatic environment from agricultural irrigation returns, wash out processes, soil erosion, domestic and industrial waste disposals as well as by direct application to the aquatic environment. Organochlorine insecticides such as p,p´-DDT, γ-hexachlorocyclohexane, dieldrin, heptachlor, and heptachlor epoxide are part of wide spectrum of pesticides which are known for their high persistence in the environment. The organochlorine pesticides were banned or restricted since a long time in most of developed countries, but some of them are still used and produced in many developing countries, for instance p,p´-DDT and hexachlorocyclohexane are still produced in India (Ahmad et al., 1996). In Jordan, p,p´-DDT is still being used in the field of public health, where 634 tons were applied over the period 1970-1993 to control the insect born-diseases, although chlorinated pesticides have been banned from agricultural use since 1985 (Nasir et al., 1998; Alawi and Ababneh, 1991; Al-Mugrabi and Qrunfleh, 2002).

Finally, chlorobenzenes (CBz) are a group of substituted monocyclic aromatic hydrocarbons. They might enter the aquatic environment as pesticides, solvents, deodorants, by-products of agro- or petrochemicals, and as contaminants of other chemical products (Beurskeus et al, 1994; Lee et al., 2000). Due to hydrophobic interactions these compounds tend to adhere to suspended particles or sediments in an aquatic environment. The present work was concentrated on the relatively low volatile CBz which are pentachlorobenzene (PCBz) and hexachlorobenzene (HCBz). Different concentrations of PCBz and HCBz have been reported in water, biota, sewage sludges, and sediments worldwide (Oliver and Nicol, 1982; Pererra et al.,

1988; Wang et al., 1995; Lee and Fang, 1997), as well as in Jordan mostly HCBz has been investigated as pesticides (Alawi and Ababneh, 1991; Al-Mugrabi and Qrunfleh, 2002).

A wide range of analytical methods have been used worldwide for identification and quantification of hydrophobic organic compounds from environmental solid samples, such as soils and sediments. Generally, the classical residue analysis can be carried out as follows: the samples are pre-treated to assure sample stability and homogeneity, then they are extracted to release target compounds out of the matrix using residue grade organic solvents. Then, the extract is subjected to clean up procedures which usually have the goal to remove the co-extractants and to separate the interfering materials. That leads to enhance the quality of the instrumental analysis which is usually came after the clean up procedure. Finally, quality control measurements are carried out for the experimental method to assure its accuracy and precision.

Chromatographic analytical methods are widely applied for the variety of environmental matrices, such as gas chromatography (GC) which can be coupled to different analytical detectors: flame ionization detector (GC/FID), electron capture detector (GC/ECD), mass spectrometer detector (GC/MS), etc.. Martens et al. (2002) have compared the several extraction techniques for determination of polychlorinated organic compounds in sediments namely Soxhlet extraction, accelerated solvent extraction, microwave-assisted extraction, fluidized-bed extraction and ultrasonic extraction. They have concluded that with respect to the analytical performance of the analytical method additional factors should be taken in consideration such as purchase costs, solvent consumption, time and handling. Classical Soxhlet extraction has been widely used to extract the HOC from environmental solid samples (Hyötyläinen and Oikari, 1999; Wu et al., 1997; Jaouen-Madoulet et al., 2000; Jiries et al., 2000). Furthermore, an exhaustive extraction at different pH values based on liquid-liquid partitioning followed by sophisticated clean up procedures for semivolatile organic compounds in sediments and sewage sludges were developed by Kolb et al. (1995). Column extraction procedures were used as Standard Operation Procedures (SOP) for the European Environmental Specimen Banking (ESB) for analysis of chlorinated hydrocarbons in environmental samples (Rossbach, 1992). Totally, the ideal choice of the analytical method might be restricted by several factors such as the sample matrix, cost, need or necessity, time and handling.

1.1 Study area and environmental prospects

Jordan is located between 29.11 – 33.22 north and between 34.59 – 39.18 east parallels and spreads over 89,342 km^2 of a divers variety of landscape. From hills and mountains of the geographic center of Jordan to the Badia eastward direction Saudi Arabia, the Jordan valley which forms the western boundary to Israel and Palestine, where Jordan River flows into the lowest point on earth (400 m below sea level). North to Jordan are located Syria and Iraq, in the south Jordan has only 25 km coastline to the Red Sea, on which the Aqaba Gulf is located (**figure 1.1**). The population of Jordan was 5.039 millions, the population growth rate 2.8 %, and the population density 56.4 capita/km^2 (Anonymous, 2000a). The estimated population by governances and the population density are presented in **table 1.1**.

Table 1.1. Estimated population by governances and the population density (Anonymous, 2000a).

Governance	Area (km^2)	Population	Population Density (capita/km^2)
Amman	8,231	1,917,300	232.9
Balqa	1,076	330,600	307.2
Zarqa	4,080	792,600	194.3
Madaba	2,008	128,500	64.0
Irbid	1,621	899,000	554.6
Mafraq	26,435	232,300	8.8
Jarash	0,402	148,100	368.5
Ajlun	0,412	111,900	271.5
Karak	3,217	202,700	63.0
Tafiela	2,114	76,500	36.2
Maán	33,163	98,200	3.0
Aqaba	6,583	101,300	15.4
The Kingdom	89,342	5,039,000	56.4

The study area is located to the northeast part of the country, which is presented by Zarqa River basin and spreads over 3900 km^2, while the river catchment area extended

from Jabel Druz to the Jordan River which measures 4025 km^2 and its average annual precipitation is 237 mm. The source of Zarqa River is Amman city at Ras´ Al Ayn spring, where it starts as Seil Zarqa and flows northeast Amman city, then passes Zarqa city and leaves the urban area to join Wadi Dhuleil near Assukhana, it turns west to flow via King Talal Reservoir (KTR). Downstream of KTR, it joins Jordan River and their waters are used for irrigation purposes (**figure 1.6**). The average annual discharge of Zarqa River was 64.88 million m^3/year until 1976, after that the annual discharge has been changed due to construction of KTR in 1977 and establishment of As-Samra WSPs in 1985 (Salameh and Al-Ansari, 2000).

About 52 % of the Kingdom's population and more than 80 % of the national industries are located within the study area. Zarqa River is considered as environmental sink for most of pollutants that could be released into the environment from the different anthropogenic activities. However, it is receiving its water from precipitation during wet season, As-Samra WSPs effluents, agricultural irrigation returns, as well as from untreated industrial and domestic wastewater effluents. **Figure 1.7** shows untreated domestic wastewater leakage from the transport pipeline to the As-Samra wastewater stabilization ponds (WSPs) and **figure 1.8** represents direct discharge of industrial waste into river drainage system. As-Samra WSPs is playing an important role in the contamination of the aquatic system of Zarqa River and the groundwater aquifers. It is located in the Hashimyya area and serves Amman and Zarqa governances. The plant was designed to receive 70,000 m^3/day, but at present it is overloaded and receives more than 170,000 m^3/day (Saliba et al., 1999; WAJ, 2000). The performance of As-Samra waste stabilization pond system has been studied and found out that the ponds are overloaded, and the failure of the system to meet its treatment objectives resulted from poor projection of local data and design criteria (Shanableh, 1996). Its effluent is discharged into a stream bed that runs 1.5 km before it has been discharges into Wadi Dhuleil which runs in a shallow channel for about 12 km to join Seil Zarqa at Assukhana area and to form Zarqa River. Water quality of As-Samra effluents as well as along Zarqa River are continually monitored by the Water Authority of Jordan (WAJ). Influents and effluents quality of As-Samra in addition to some selected pollution indicators along Wadi Dhuleil and Zarqa River are summarized in **table 1.2**.

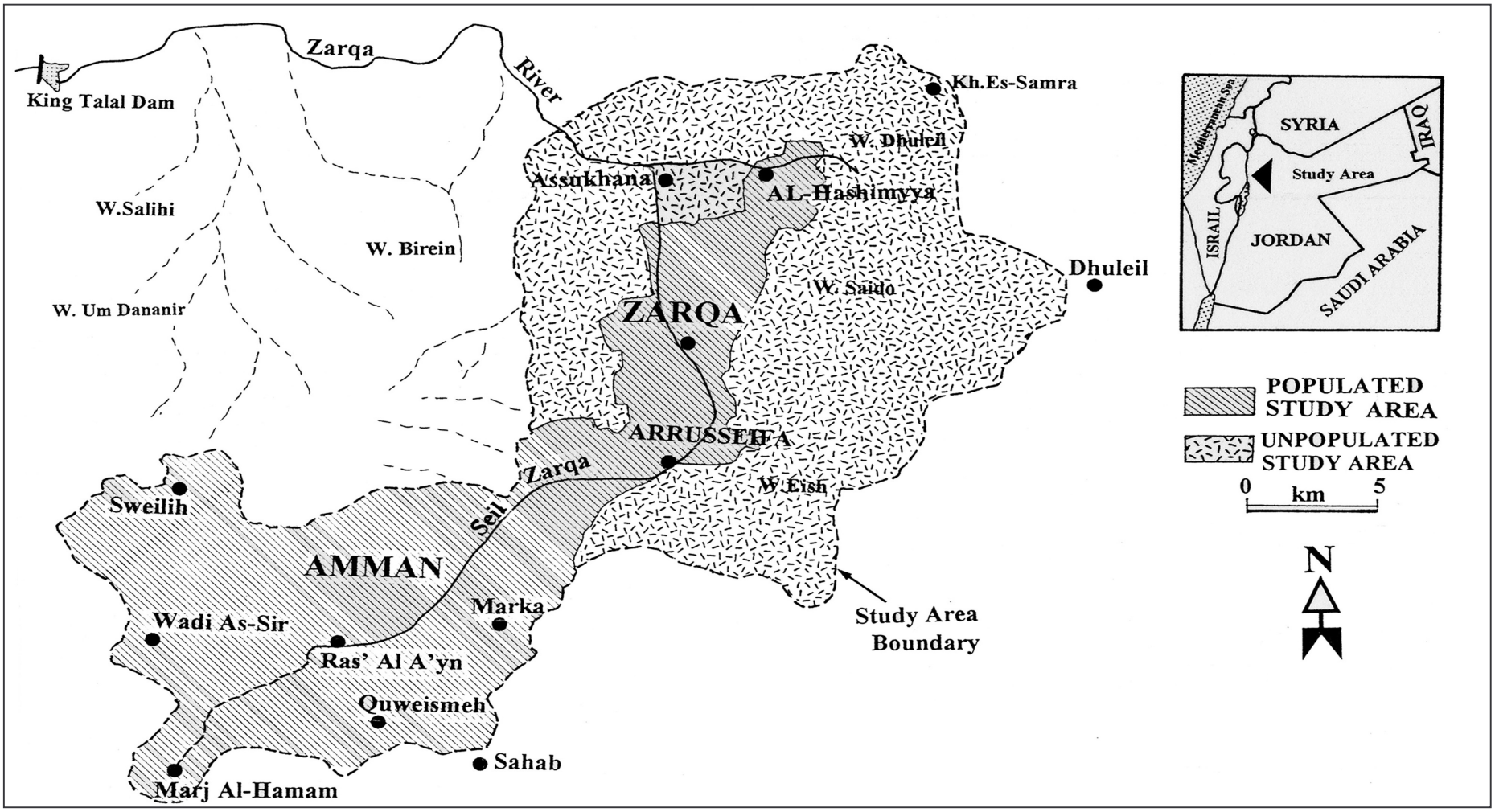


Figure 1.6. Distribution of population in study area.

Figure 1.7. Untreated wastewater leakage from the transport line to As-Samra WSPs.

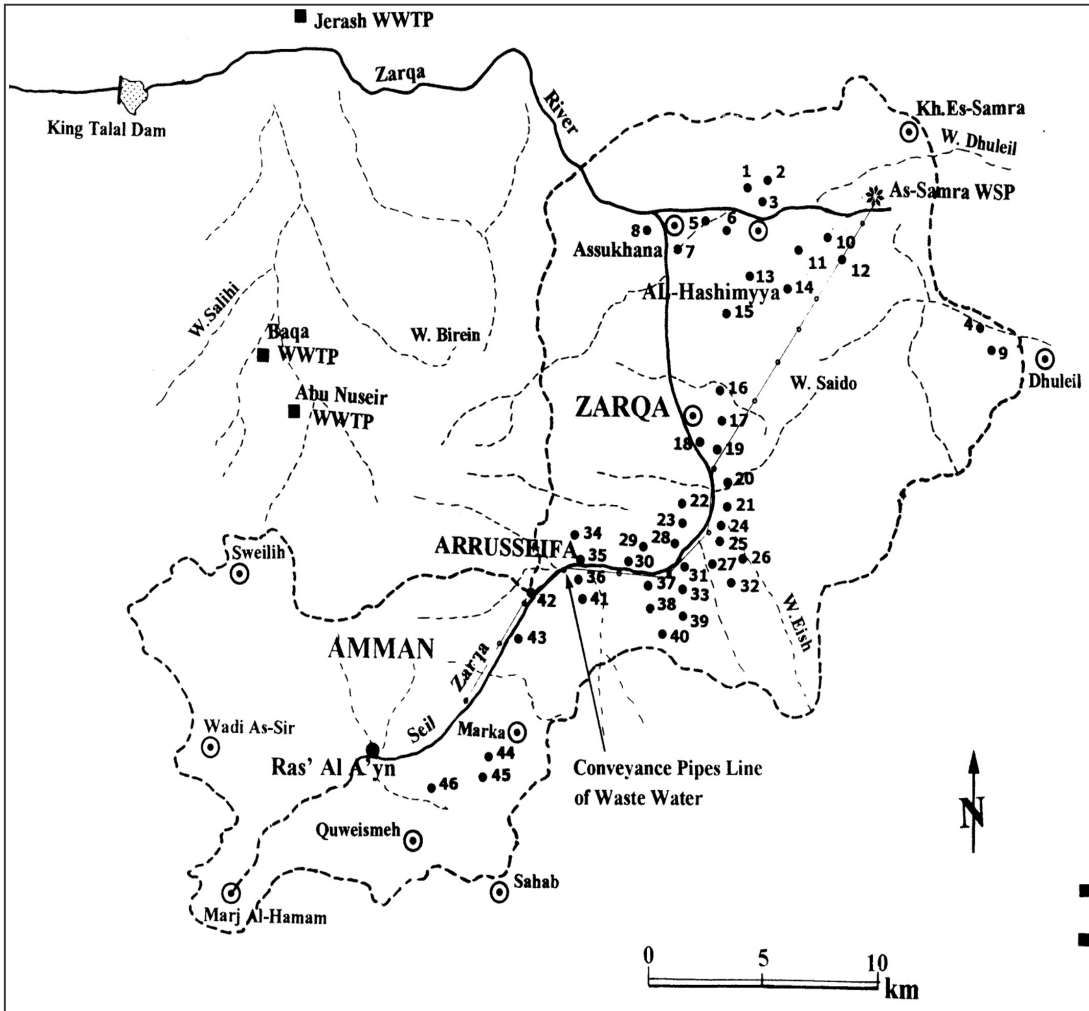
Figure 1.8. Industrial effluents discharged directly into river drainage system.

Table 1.2. Technical data and some selected water pollution indicators for As-Samra WSPs, Wadi Dhuliel, and Zarqa River (WAJ, 2000; Anonymous, 2000b).

Parameters	Unit	Inlet	Outlet
Flow	m^3/d	170,752	149,589
pH	SU*	7.18	8.05
TDS	mg/L	1279	1220
TSS	mg/L	528	146
BOD_5	mg/L	698	139
COD	mg/L	1786	497
NH_4	mg/L	62	89
Total-P	mg/L	18	19
B	mg/L	0.55	0.71
Cl	mg/L	374	389
Ni	mg/L	NA**	0.05
Zn	mg/L	NA	0.20
Cr	mg/L	NA	0.05
Pb	mg/L	NA	0.05
Mn	mg/L	NA	0.08
Cd	mg/L	NA	0.03
Cu	mg/L	NA	0.02
Fe	mg/L	NA	0.27
ΣPAH	µg/L	1.33	0.68
ΣPAH Wadi Dhuleil	µg/L	-	0.45
ΣPAH Zarqa River	µg/L	-	0.22
Chlorinated pesticides	µg/L	ND***	ND

*SU :Scale Unit,** NA : not analyzed, *** ND : not detected.

Amman-Zarqa area is the main industrial center in Jordan. Its rapid economic, industrial, and population growth have been enhanced the environmental stress on Zarqa River. More than 166 different industries ranged from light to intermediate industries are located in Zarqa River basin and about 26 from these industries located along their banks (Dallal et al., 1999), such as Jordanian Oil Refinery, Al-Hussien thermal power station, phosphate mining, textile industries, paper mills, rubbers, plastics, batteries, paints, steel and casting industries, tanning, detergents, sulfo-chemicals and petrochemicals industries, veterinary medical products and pesticides industries, breweries and distilleries industries, automobile repairing and maintenance industries. The area includes also many open dumps and sanitary landfills. **Figure 1.9** presents distribution of main industries in Zarqa River basin.



No	FACTORY
1	STEEL FACTORY
2	JORDAN PIPES MANUFACTURING CO.
3	HASHEMITE FLOUR MILL. AMMAN
4	JAMALFLOUR MILL AMMAN
5	NATIONAL INDUSTIES (TISSUE PAPER)
6	INTERNATIONAL CERAMIC
7	SHAFA FOOD NAT.IND
8	JORDAN IRON & STEEL IND.CO.
9	INDUSTRIAL COMMERCIAL & AGRICU.
10	JORDAN PETROLEUM REFINERY CO.
11	UNITED INDUSTRIES CO.
12	AL –HUSSEIN POWER STATION
13	KAWTHER BOTTLING CO.
14	MODERN FLOUR MILL MAHATTA
15	SULPHOCHEMICAL CO.
16	JOR. ICE & AERATED WATER CO.
17	JORDAN WORSTED MILLS CO.LTD.
18	JORDAN TANNING CO.LTD.
19	EAGLE DISTILLERIES CO.
20	JORDAN FOOD PROCESSING CO.
21	ATLAS PAPER CO.
22	MIDDLE EAST PHARMACEUTICAL CO.
23	JORDAN INDUSTRIES FOR BRICKS

No	FACTORY
24	ARAB WHITE CEMENT INDUSTRIES
25	PETRA IRON CO. HASHIMYYA
26	JORDAN SPINNING CO.
27	NATIONAL INDUSTRIES (GHREISE)
28	SUBHI JABRI & SONS CO.
29	JORDAN PIPES MANUFACTRING CO.
30	JORDAN BREWERY CO LTD.
31	J.TILES CO/M.KRAIDLY
32	SUBHI JABRI & SONS CO.
33	MODREN DAIRY CO.
34	MINERAL RESEARCH RUSEIFA
35	ARAB ALUMINUM IND.CO.LTD.
36	DANISH JORDANIAN DAIRY CO.
37	JORDAN PAPER & CARDBOARD MFG.
38	ARAB DAIRY CO.
39	MAFRAQ AGRICULT. CO.
40	JORDAN CERAMIC INDUSTRIES CO.
41	NATIONAL MINERIAL WATER CO.
42	ARAB BREWERIES CO.LTD.
43	JORDAN PORCELAIN CO.
44	HAYMOUR COUSINS CO.
45	NATHEER MOH.SULTAN
46	JORDAN STEEL /BADRAN

■WSP Waste Stabilization pond.

■WWTP Waste Water Treatment Plant

Figure 1.9. Industries along Zarqa River.

The study area was divided into three categories, based on the geographical location and dominated anthropogenic activities. Firstly, Seil Zarqa category (Z1-Z10), which passes Amman and Zarqa governances and influenced by industrial, municipal, and agricultural activities. Secondly, Wadi Dhuleil category (D1-D4) which was affected mainly by the treated wastewater effluent of As-Samra WSPs. Thirdly, R category (R1-R3) represents the Zarqa River itself after co-effluence of Seil Zarqa (Z) and Wadi Dhuleil (D). Totally, the whole drainage system of the area investigated is affected by agricultural, municipal, and industrial activities.

The industrial wastewater effluents are controlled and regulated by the Water Authority of Jordan (WAJ) according to the Jordanian Industrial Wastewater Standards (JIWS) number (202/1990) (Anonymous, 2000b). The annual report for the year 2000 for the water quality in Jordan has been proved that most of the industries located in Amman-Zarqa area were not satisfied the JIWS, therefore, the quality of the industrial wastewater in the area is not suitable to discharges into streams or to be used for agriculture (WAJ,2000). Most factories are owning their internal wastewater treatment plants and about 50 % from these industries are connected to the domestic sewer system via the wastewater transport pipeline to As-Samra WSPs. However, the rest are discharging their effluents into the Zarqa River drainage system or far away into different dumping sites (WAJ, 2000). An idea about the industrial wastewater quality for selected industries compared to the JIWS are given in **table 1.3**.

1.2 Climate and rainfall quantities

Jordan is characterized by the Mediterranean climate which is revealed by hot, dry, sunny summers, and cool rainy winters. The average temperatures are around, 28-25 ^{o}C for summer and 8-10 ^{o}C for winter. More than 80 % of Jordan area is classified as arid and about 20 % is semiarid, Jordan depends mainly on precipitation as main source of water. The average rainfall ranges from 600 mm/year in the north to less than 50 mm/year in the south and east parts of the country. The seasonal rainfall usually occurs from December until March. The eastern catchment area of Zarqa River receives an average annual precipitation of 182 mm, the middle part, between the eastern catchment and the western highlands, holds an average of 243 mm/year. The western catchment including the highlands and the Jordan Valley area receives an average of 397 mm/year (Salameh, 1996).

Table 1.3. Example of selected parameters to show the industrial wastewater effluents quality which are located in Amman-Zarqa area compared to JIWS number (202/1990), (Anonymous, 2000c).

Test	Unit	JIWS	Detergents	Yeast	Textile	Petro-chemicals	Slufo-chemicals	Paints	Pharmaceuticals
pH	SU	6.5-9.0	11.29	6.49	4.35	7.19	6.77	7.68	6.59
DOC	mg/L	>1.0	2.6	2.8	3.5	2.6	2.2	2.4	3.3
TDS	mg/L	<3000	5983	13321	2983	240	50597	5128	667
TSS	mg/L	<50	485	1188	51	6	853	56	9470
BOD_5	mg/L	<50	4186	6949	428	1548	2184	1554	8099
COD	mg/L	<150	11868	14799	987	2816	72597	4201	22178
MBAS	mg/L	<25	215.2	4.9	12.4	2.3	1807.3	11.0	0.2
NO_3-N	mg/L	<12	NA	NA	NA	NA	NA	3.8	0.7
NH_3	mg/L	<5.0	5.2	89.7	81.3	10.8	12.0	5.4	<1
Cl	mg/L	<500	1403	886	962	70	778	130	194
SO_4	mg/L	<500	NA	NA	NA	NA	NA	1470	83
FOG	mg/L	<5.0	2816	5139	13	115	211	75	17021
PO_4-P	mg/L	<15	20.18	NA	4.93	0.70	2.71	1.63	0.07
Phenol	mg/L	<0.002	0.16	0.51	0.046	0.17	NA	NA	<0.005
B	mg/L	<1.0	0.17	0.19	0.18	< 0.05	0.17	0.11	0.17
CN	mg/L	<0.1	NA	0.08	<0.03	NA	NA	<0.03	<0.03
Al	mg/L	<5.0	4.3	0.95	108.55	0.20	0.80	5.10	9.10
As	mg/L	<0.05	<0.005	<0.005	0.01	<0.005	NA	NA	<0.005
Cd	mg/L	<0.01	<0.003	<0.003	<0.003	<0.003	NA	<0.003	<0.003
Cr	mg/L	<0.1	0.13	0.13	0.07	0.07	1.04	0.04	0.30
Cu	mg/L	<2.0	0.05	0.09	<0.025	<0.025	NA	<0.025	0.67
Fe	mg/L	<1.0	7.28	3.14	2.05	3.18	11.33	1.49	6.68
Hg	mg/L	<0.001	<0.001	<0.001	<0.001	<0.001	NA	NA	<0.001
Mn	mg/L	<0.2	0.25	0.27	0.09	1.77	0.22	<0.05	0.17
Ni	mg/L	<0.02	0.05	0.17	<0.02	<0.02	0.37	<0.02	<0.02
Pb	mg/L	<0.1	0.19	<0.01	<0.01	<0.01	NA	<0.01	0.30
Se	mg/L	<0.02	0.01	0.01	<0.005	<0.005	NA	NA	0.16
Zn	mg/L	<15	0.87	0.29	0.56	0.03	1.01	0.18	3.03

*NA : not analyzed.

The cumulative rainfall quantities in mm from four meteorological stations which are located in the Zarqa River basin for the periods: from 14.10.2000 to 23.03.2001, and

from 28.10.2001 to 29.03.2002 are presented in **figures 1.10** and **1.11**, respectively. The first sampling activity was carried out in December 12-17, 2000 and aimed for sampling sites orientation and analytical method development. The samples were collected after average cumulative rainfall of 26 mm which can be categorized as first rainfall events after summer season. **Figures 1.10** shows the rainfall quantities and their average from 14 October 2000 to 23 March 2001, where the average cumulative rainfall for the four meteorological stations reached 157 mm at the end of the season. However, the sampling activities for the main field monitoring study were carried out two times and they are presented in **figure 1.11** consequently. The first time in November 22-26, 2001 represented the end of summer season, which was carried out after 13 mm as average cumulative rainfall events. This sampling period might be came after short wash out events in the studied area. The second time on January 26-29, 2002 represented the winter season after several wash out events. The cumulative average rainfall quantities at the repeated sampling campaign was 171 mm and it reached 240 mm at the end of the season. The results are discussed later depending on the seasonal classification as two sampling campaigns, the first campaign represents the summer season (November, 2001) and the second campaign (January, 2002) represents the winter season after several wash out processes.

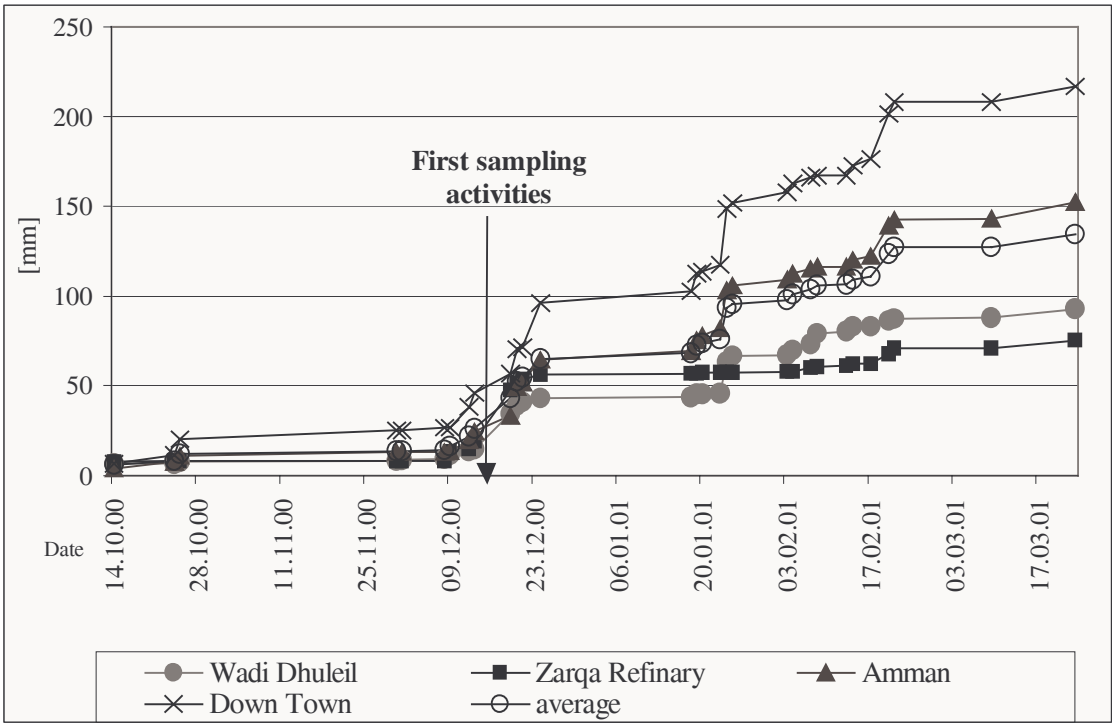


Figure 1.10. Cumulative rainfall quantities in mm from four meteorological stations and their average at the Zarqa River basin for the period from 14.10.2000 to 23.03.2001 (Metrological Department, 2003).

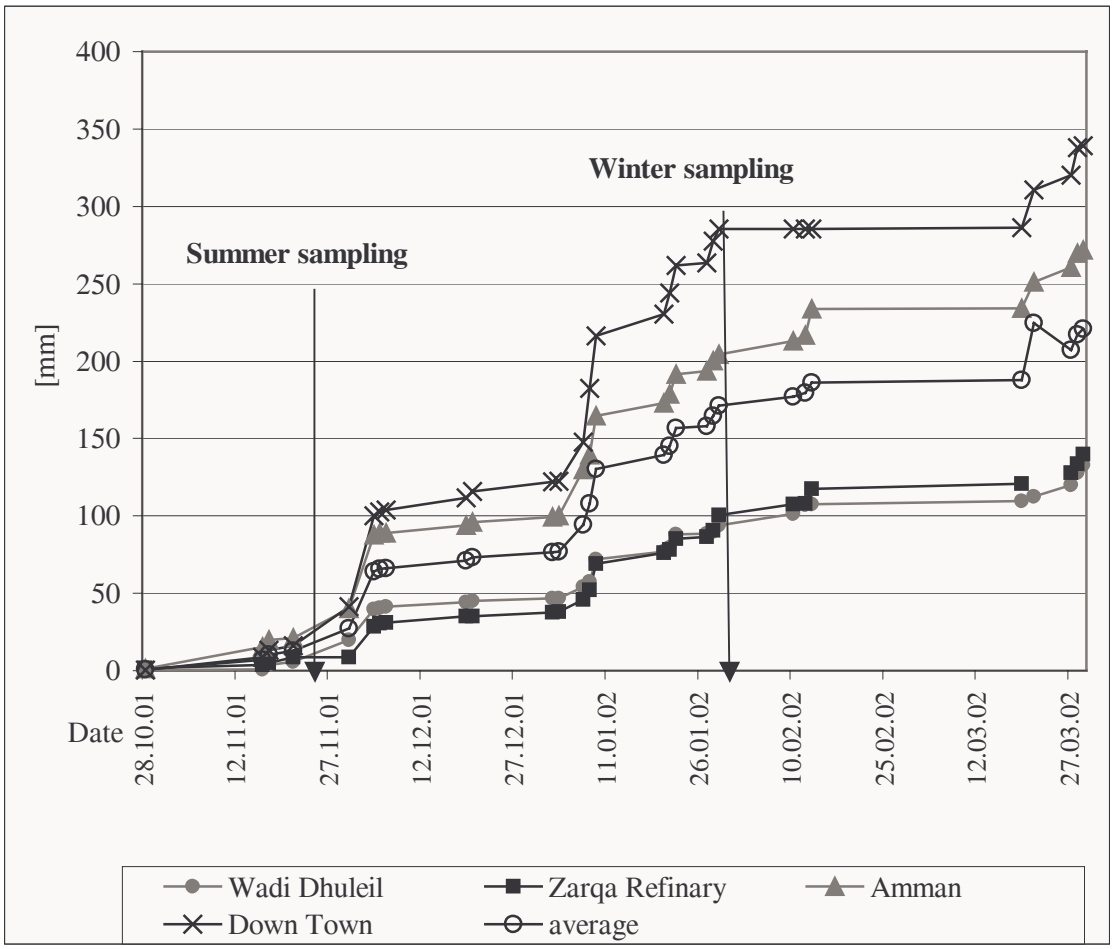


Figure 1.11. Cumulative rainfall quantities in mm from four meteorological stations and their average at the Zarqa River basin for the period from 28.10.2001 to 29.03.2002 (Metrological Department, 2003).

1.3 Previous studies

Numerous studies of inorganic contaminants along Zarqa River were conducted and all emphasized a deterioration of the environmental quality (Tutunji et al., 1986; El-Khattari, 1986; Nawafleh, 1992; Amrat, 1992; Al-Jundi, 2000). However, the state of organic contamination of the Zarqa River ecosystem is not known yet. Generally, limited number of studies concerning organic contamination in Jordanian environment have been performed. For example, the polychlorinated dibenzodioxins and furans have been studied on a municipal open combustion landfill site nearby Amman (Alawi et al.,1996), PAH in wastewater, sediment, sludge, and plants in south of Jordan were investigated (Jiries et al., 2000). In addition, PAH, chlorinated pesticides, and phenols have been studied in different water bodies in Jordan. This study was supported by the

European community under project number (SEM/03/628/033) in the period 1999-2000. However, no environmental relevant concentrations of the target organic compounds were detected in the analyzed water samples. In addition, the quality of rain and water and sediments of street runoff in Amman area were investigated of their content of inorganic constituents and polynuclear aromatic hydrocarbons (Jiries et al., 2001; Jiries et al., 2003), where the total concentration of PAH ranged from 46.1 to 974.8 ng/L and from 65.9 to 1420.8 ng/L for rain and street runoff, respectively. Despite of, a lack of the background data can still be observed about the occurrence of PAH, PCB, and CBz in the Jordanian environment.

On the other hand, organochlorine pesticides residues were studied in different Jordanian environments (Alawi et al., 1990; Alawi and Ababneh, 1991; Alawi et al., 1995; Nasir et al., 1998; Al Nasir et al., 2001; Al-Mughrabi and Qrunfleh, 2002). Most of the previous studies were approved that Jordanian environment is contaminated with organochlorine pesticides, which were used in Jordan for more than 40 years, before they had been banned from agricultural use in the period 1980-1985. However, some of these organochlorine pesticides are still used in Jordan for public health purposes, such as p,p´-DDT. For instance, environmental relevant concentration of p,p´-DDT (4.05 mg/kg) and p,p´-DDE (0.01-0.46 mg/kg) were detected in soil samples from Jordan Valley (Al-Mughrabi and Qrunfleh, 2002). The existing data for Jordan as well as from different countries are compared later with the findings of the present work.

1.4 Objectives

The lack of monitoring studies and environmental background data concerning organic pollutants of Zarqa River basin has initiated the present work. It is obvious that many pollutants related to municipal, industrial, and agricultural activities are worsening the ecosystem investigated, especially after operating the largest wastewater stabilization ponds in Jordan (As-Samra WSPs) which caused the deterioration in the water quality along Zarqa River as well as in King Talal Reservoir. Semivolatile organic compounds such as PAH, PCB, CBz, and organochlorine pesticides adsorb onto streambed sediments and can persist in the environment for many years. In addition, they have high bioaccumulation potentials. Studying their occurrence and distribution pattern can be contributed to their origin, assessment the environmental quality as well as measurements the environmental background concentration.

The preliminary work aimed at orienting on the possible prevalent environmental contaminated sites as well as at highlighting the hot spots along Zarqa River waters and sediments. This aim could be achieved by performing environmental analysis for selected sites using well examined analytical procedures such as slurry extraction (S19 multi-method) followed by gas chromatography with mass spectroscopy (GC/MS) screening analysis. It was further aimed at continuing the development and optimization a convenient analytical procedure to meet the samples matrix requirements for simultaneous investigation of a wide range of hydrophobic organic pollutants in river sediment from semi-arid to arid environments, which are heavily loaded with domestic and industrial wastewater effluents.

After analytical method development and sampling orientation, a field monitoring study should be conducted to investigate the concentration levels and the seasonal distribution pattern of xenobiotics in order to evaluate the environmental quality. In addition, this work was aimed at characterizing the sediments pollution profiles which could be used for a preliminary assessment of the possible sources and pathways of the present organic pollutants.

The present work is the result of German and Jordanian institutional research cooperation. The Institute of Ecological Chemistry and Waste Analysis at the Technical University of Braunschweig and the German Catholic Academic Exchange Services (KAAD) have been supported the present work technically and financially. On the other hand, the Department of Environmental Geology and Hydrogeology at Jordan University and the Department of Soil at Mutah University supported the sampling activities and samples preparation in Jordan. Project stages and institutional cooperation are presented in **figure 1.12**.

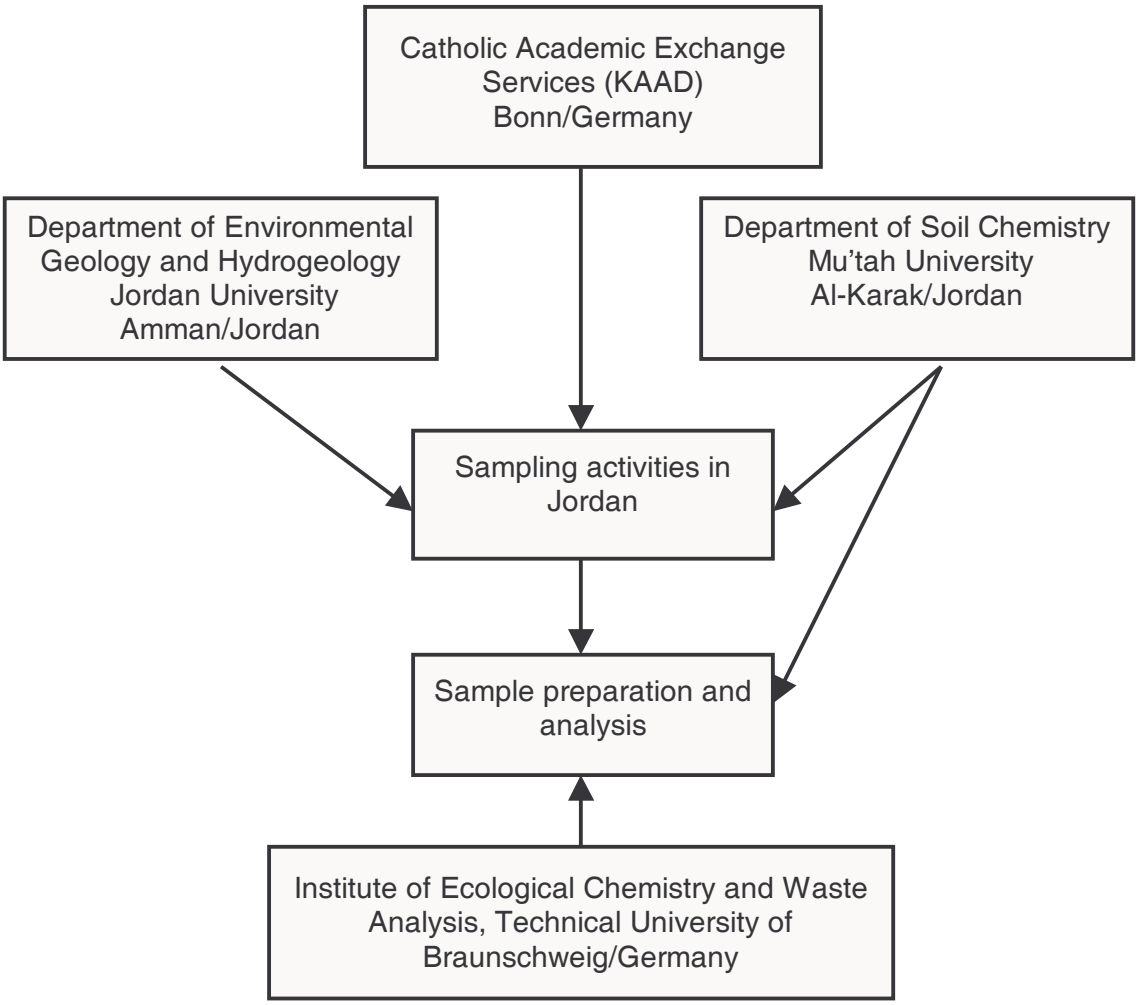


Figure 1.12. Project stages and institutional cooperation.

2. Experimental

2.1 Sampling strategy and technique

The first sampling activities were carried out in December 2000, to get samples for analytical method development and for first orientation on the possible prevalent environmental pollutants. In the second sampling period twenty sediment samples were collected along Zarqa River (R) and its main tributaries namely Seil Zarqa (Z) and Wadi Dhuliel (D). As the annual rainfall occurs usually in the period from December to March, samples were collected during November 22-26, 2001, and in order to cover the seasonal variation, the sampling campaign was repeated in addition to extra sample collected along Zarqa River in January 26-27, 2002. Besides these, reference site was taken 120 km south of Amman far away from heavy anthropogenic activities, and industrial waste disposal site which was located at Wadi Dhuleil tributary.

Mixed surface sediment samples (0-5 cm) were collected from one square meter at each bank of the drainage system pooled and homogenized to get representative samples. They were stored in glass jars until transported to the lab, pre-treated and stored at –20 ^{o}C until analysis. **Figures 2.1** and **2.2** exemplify the sampling technique and cross-section of the sediment profile, respectively. In case of Seil Zarqa and Zarqa River, the sediment profiles were characterized by two sediment layers. The upper layer had very thin black color, while, the lower one was brown colored (mostly of sandy clay loam texture). In case of Wadi Dhuliel tributary, the sediment profiles were characterized by sandy loam mixed with fine sewage sludge sediments originated from effluents of As-Samra wastewater stabilization ponds (WSPs).

Crude stable sediment extracts were prepared in the Department of Soil Chemistry at Mu'tah University/Karak/Jordan and then transported to Braunschweig under cold conditions. Clean up procedures and the analyses were performed in the Institute of Ecological Chemistry and Waste Analysis of the Technical University of Braunschweig. Symbol W was added to all sample codes which were collected during January, 2002. The sampling sites along Zarqa River and its tributaries are presented in **figure 2.3**.

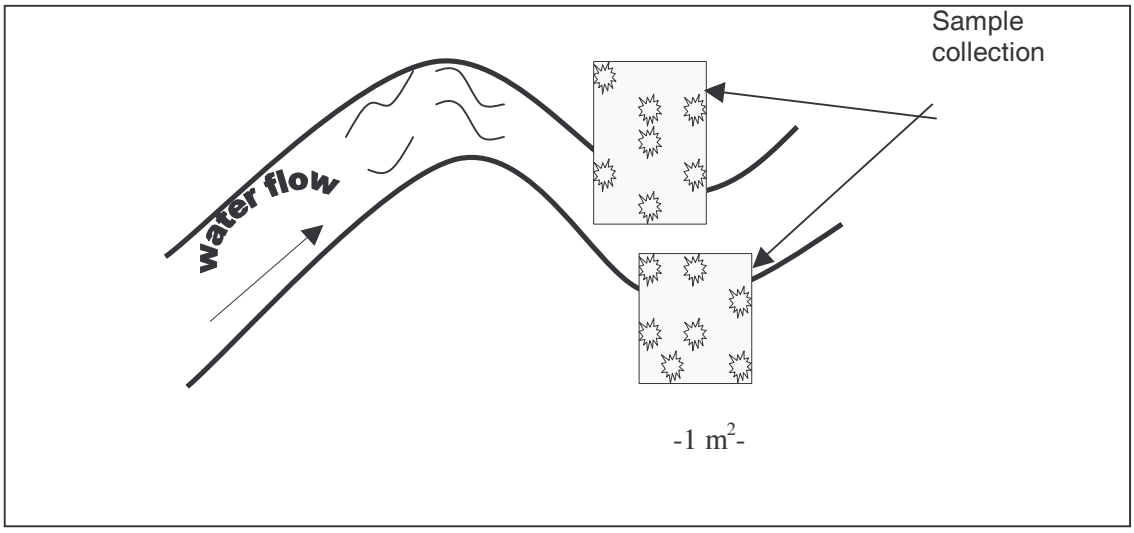


Figure 2.1. Sampling strategy at each site.

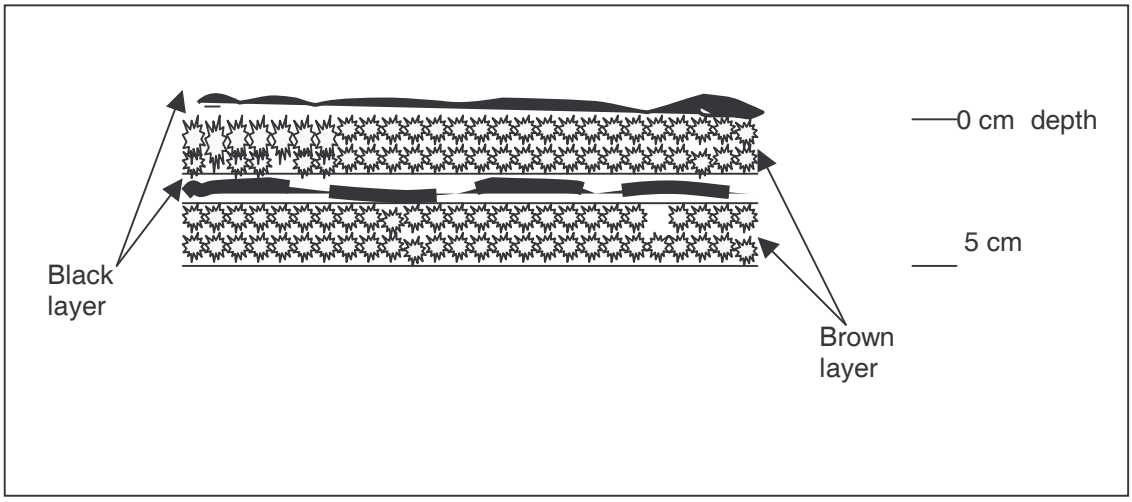


Figure 2.2. Sedimentation profile and sampling depth.

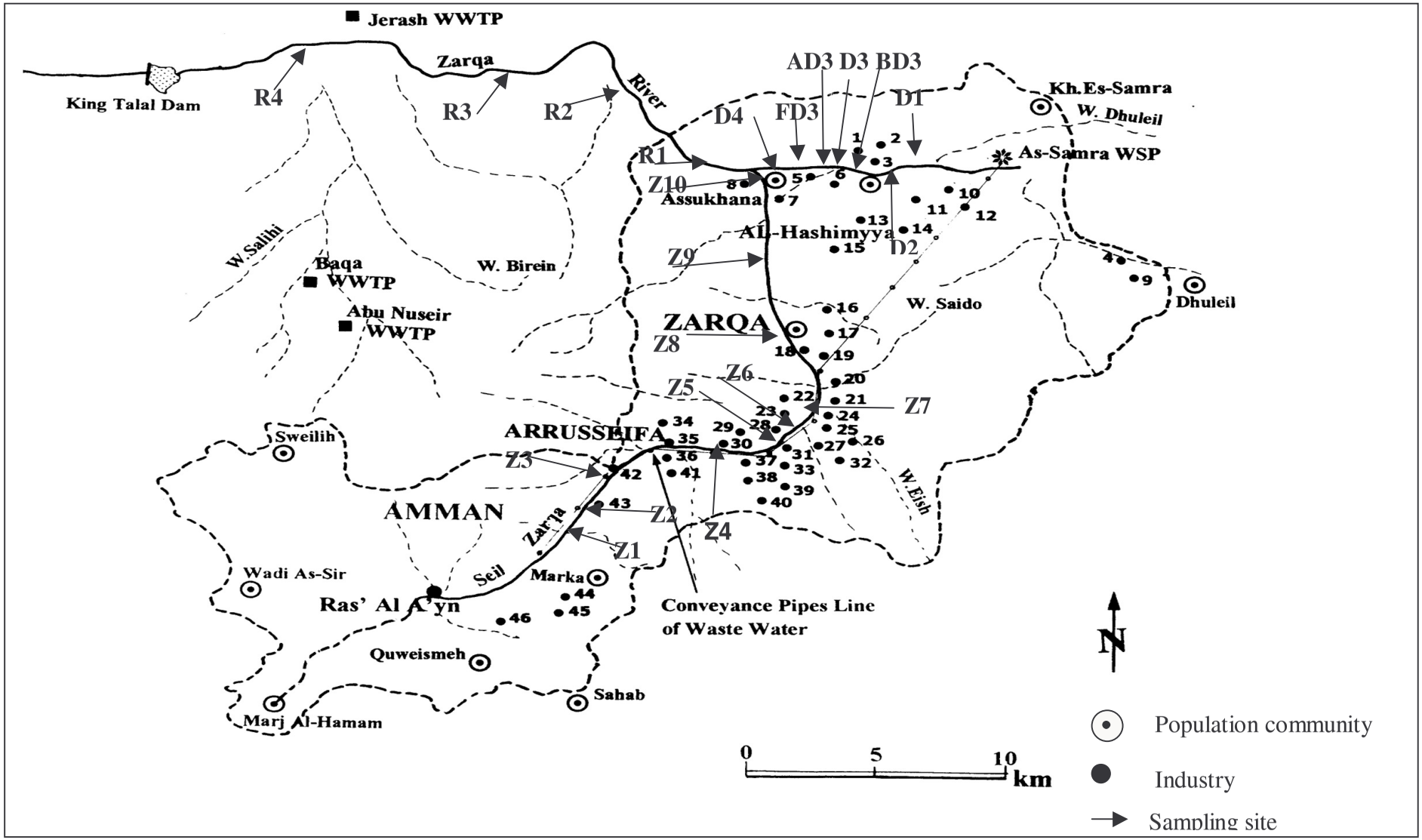


Figure 2.3. Sampling sites.

2.2 Chemicals

The chemicals used were classified into three classes: reference materials, chemical substances and laboratory chemical reagents, and solvents.

2.2.1 Reference materials

Reference laboratory materials were used for identification and quantification of the target compounds, they are listed in **table 2.1**. Stock solutions were prepared of each individual solid reference materials of 1 µg/µL either in n-hexane or methanol.

Table 2.1. Reference laboratory materials.

Reference substance	Abbreviation	Company
PCB 28 (Purity >99.9)	PCB 28	Promochem, Germany
PCB 52 (Purity >99.7)	PCB 52	Promochem, Germany
PCB 101 (Purity >99.8)	PCB 101	Promochem, Germany
PCB 153 (Purity >99.8)	PCB 153	Promochem, Germany
PCB 138 (Purity >99.5)	PCB 138	Promochem, Germany
PCB 180 (Purity >99.6)	PCB 180	Promochem, Germany
1,2,3,4-tertachloronaphthalene	1,2,3,4-TCN	Promochem, Germany
USEPA 16 PAH (100 ng/µL)	PAH	Promochem, Germany
Pentachlorobenzene (>99%)	PCBz	Riedel-de Haën, Germany
Hexachlorobenzene (>99%)	HCBz	Riedel-de Haën, Germany
α–hexachlorocyclohexane (97.8%)	α–HCH	Dr. Ehrenstorfer, Germany
β–hexachlorocyclohexane (99.5 %)	β–HCH	Dr. Ehrenstorfer, Germany
γ-hexachlorocyclohexane (99.1 %)	γ– HCH	Dr. Ehrenstorfer, Germany
δ–hexachlorocyclohexane (98.4 %)	δ–HCH	Dr. Ehrenstorfer, Germany
trans-heptachlor epoxide (10 ng/µL)	trans-h. epoxide	Dr. Ehrenstorfer, Germany
cis-heptachloro epoxide (10 ng/µL)	cis-h. epoxide	Dr. Ehrenstorfer, Germany
Dieldrin (98.5 %)	Dieldrin	Dr. Ehrenstorfer, Germany
o,p´-DDE (99. 9%)	o,p´-DDE	Dr. Ehrenstorfer, Germany
p,p´-DDE (99.9%)	p,p´-DDE	Dr. Ehrenstorfer, Germany
o,p´-DDD (99.6 %)	o,p´-DDD	Dr. Ehrenstorfer, Germany
p,p´-DDD (98.8 %)	p,p´-DDD	Dr. Ehrenstorfer, Germany
Heptachlor (>99.0 %)	Heptachlor	Riedel-de Haën, Germany

2.2.2 Chemical substances

Chemical substances and laboratory reagents were used for extraction, clean up, titration, and other analytical procedures. They are presented in **table 2.2**.

Table 2.2. Chemical substances and laboratory reagents.

Chemical substance	Abbreviation	Company
Ammonia (25%)	NH_3	Riedel-de Haën, Germany
Anhydrous sodium sulfate (>98%)	Na_2SO_4	ROTH GmbH, Germany
Extra pure sea sand	Sea sand	Merck, Germany
Tetrabutyl ammonium sulfate (>97%)	TBAS	Fluka, Switzerland
Sodium sulfite AR	Na_2SO_3	Merck, Germany
Aluminium oxide 90 active neutral, 70-230 mesh	Alumina	Merck, Germany
Silica gel 60, 70-230 mesh	Silica gel	Merck, Germany
Bio-beads S-X8, 200-400 mesh	Bio-beads S-X8	Bio-Rad, USA
Potassium dichromate (99.5%)	$K_2Cr_2O_7$	Riedel-de Haën, Germany
Ferrous ammonium sulfate hexahydrate (99%)	$(Fe(NH_4)_2(SO_4)_2.6H_2O)$	Riedel-de Haën, Germany
Sodium hexametaphosphate	Calgon	Fluka, Switzerland
Sulfuric acid	H_2SO_4	Frutarom, UK
Phosphoric acid (85%)	H_3PO_4	BDH, UK
Hydrochloric acid (35.4%)	HCl	BDH, UK
Diphenyl amine indicator	For TOC	BDH, UK
Hydrogen peroxide (35%)	H_2O_2	Riedel-de Haën, Germany
Oxalic acid	$H_2C_2O_6$	Fluka, Switzerland

2.2.3 Solvents

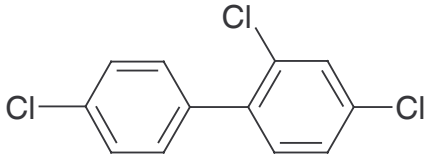
Most solvents used were of residual grade which means they were limited from ECD and FID interferences materials. These solvents are listed in **table 2.3**.

Table 2.3. The used solvents.

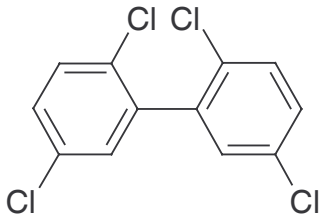
solvent	Grade	Company
n-Hexane	residual grade	Merck, Germany or Lab scan, Ireland
Acetone	residual grade	Merck, Germany or Lab scan, Ireland
Ethyl acetate	residual grade	Merck, Germany
Cyclohexane	residual grade	Merck, Germany
Methanol	residual grade	Merck, Germany
Iso-propanol	99.8 %	Riedel-de Haën, Germany
Dodecane	99.0 %	Acros, USA
Milli-Q water	<0.05 µS	-

2.2.4 Chemical structures of the target compounds

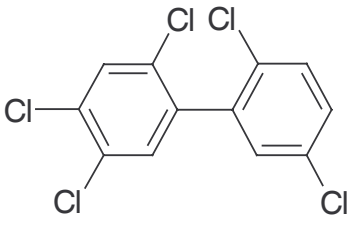
The chemical structures of the target compounds and their metabolites are presented in **figures 2.4** and **2.5**.



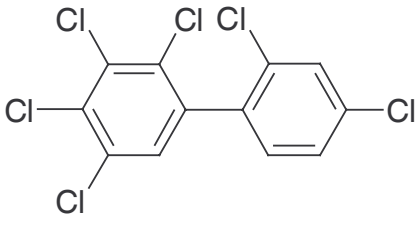
PCB 28 (2,4,4´-Trichlorobiphenyl)



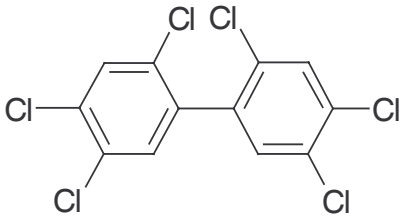
PCB 52 (2,2´,5,5´-Tetrachlorobiphenyl)



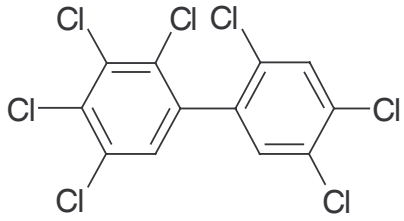
PCB 101 (2,2´,4,5,5´-Pentachlorobiphenyl)



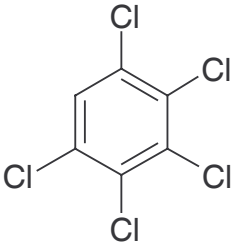
PCB 138 (2,2´,3,4,4´,5´-Hexachlorobiphenyl)



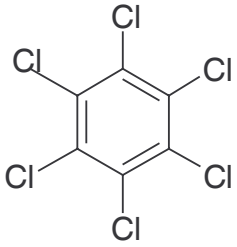
PCB 153 (2,2´,4,4´,5,5´-Hexachlorobiphenyl)



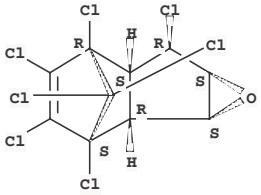
PCB 180 (2,2´,3,4,4´,5,5´-Heptachlorobiphenyl)



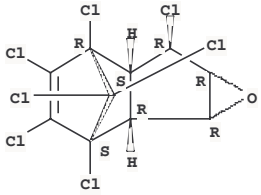
Pentachlorobenzene (PCBz)



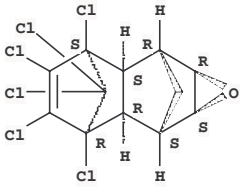
Hexachlorobenzene (HCBz)



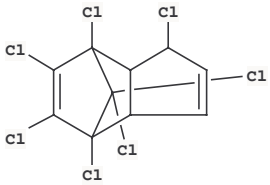
Cis-heptachlor epoxide



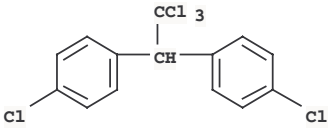
Trans-heptachlor epoxide



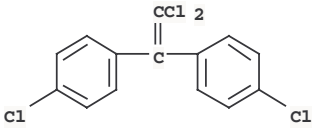
Heptachlor



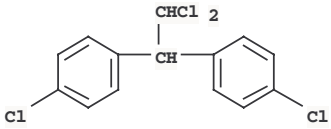
Dieldrin



p,p´-DDT



p,p´-DDE



p,p´-DDD

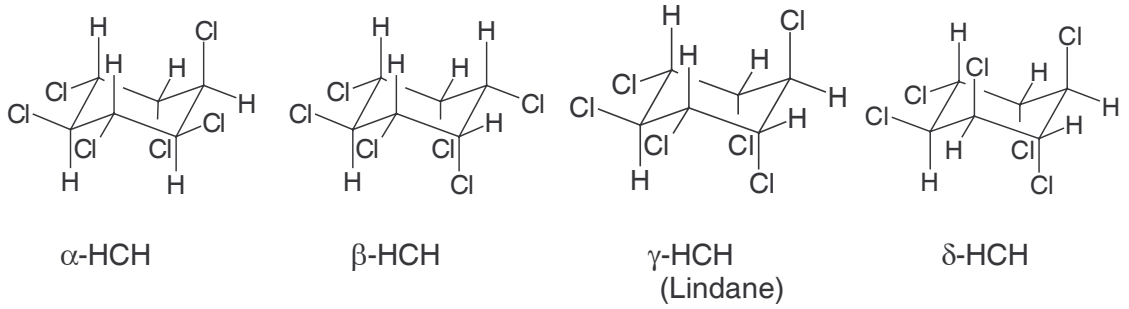


Figure 2.4. Chemical structures of organochlorine and related compounds (relative stereochemistry).

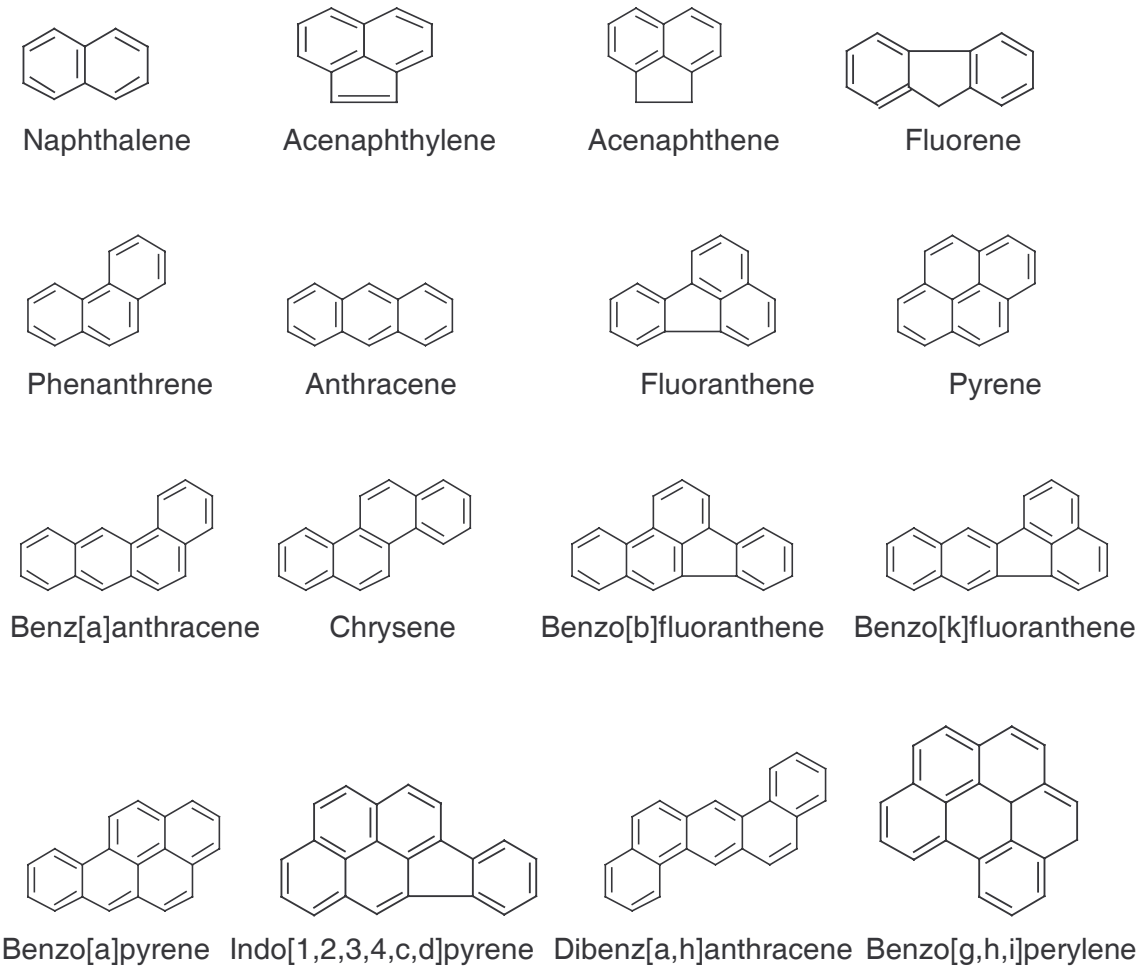


Figure 2.5. Chemical structures of 16 PAH.

2.3 Instruments and laboratory equipments

Description of the analytical instruments used are given in details for each identification and quantification procedures.

2.3.1 Gel permeation chromatography (GPC)

The Gilson GPC unit consists of isocratic HPLC-pump model 302, auto-sampler injector model 231, dilutor model 401, fraction collector model 201, and glass chromatography column filled with 38-39 cm of bio-beads S-X8 (dimensions: 59 cm length, 2.9 cm inner diameter). The eluent was a mixture of ethyl acetate and cyclohexane (50:50 % v/v). The flow rate was set at 5.0 mL/min and the injection volume was 4.0 mL. The elution was programmed as 22 min to waste, then 54 min analyte fraction, finally 10 min rinsing.

2.3.2 TOC analyzer

The Dohrmann DC-90 Total Organic Carbon Analyzer was operated at 800 ^{o}C and coupled to a infrared gas analyzer (CO_2) ranged over 0-2500 ppm (Dohrman, USA). It was used to determine the total organic carbon in the sediments samples. The system was working under HP-PEAK 96 data operating and management software.

2.3.3 Other laboratory equipments

The vertical rotary evaporator model RE 111, vacuum controller, and PTFE pump model B-160 VACOBOX were used for sample extract concentration. They were purchased from Büchi, Switzerland. Cooling system was used model RM6 LAUDA with cooling capacity down to -20 ^{o}C and the cooling solution was ethylene glycol/water (1:1). The system was made by LAUDA, Germany. The water bath was purchased from GFL (Germany) and its temperature maintained at 40 ^{o}C. pH-meter was used model METTLER TOLEDO MP 220 coupled with combined electrode model Inlab 413 pH-NTC with pH range 0-14 at working temperature range 0-60 ^{o}C (Mettler, USA). Other laboratory equipments were used such as refrigerated centrifuge, oven, horizontal shaker, hot plate, stop watch, thermometer (–20 to 200 ^{o}C), magnetic stirrer and magnetic bar, top loading balance, high precision analytical balance with five decimals, leak detector, vials caper and vials de-caper, and PTFE disposal syringe filter holder: pore 0.45 µm and filter diameter 25 mm (Macherey-Nagel, Germany).

2.3.4 Glass ware

The used glass ware were washed with phosphate and chlorine free detergent, then dried in oven and rinsed sequentially two times with residual grade acetone and one time with n-hexane before use. The following glass ware were used: glass columns: (35 cm length, 5.7 cm inner diameter) and (30 cm length, 2.0 cm inner diameter) were used for extraction and clean up procedures, respectively. Volumetric flasks (1, 2, 5, 10 and 20 mL), graduated cylinders (10, 50, 100, 500 and 1000 mL), beakers (25, 50, 100, 600 and 800 mL), Erlenmeyer flasks (250 and 500 mL), glass syringes (5 and 10 mL), pipettes (0.5, 1.0 and 10 mL), burette with PTFE Teflon stopcock (50 mL), Teflon screw cap test tubes 10 mL, soil hydrometer ranged from 0 to 60 g/L (model ASTM E 100, 152 H, Tp. 68/68 ^{o}F), micro-liter gas tight syringes (10 , 25, 50, 100, 250 and 500 µL), stopcock with PTFE valve to build up the chromatography columns by the glass bluer, porcelain mortar (capacity 500 g), 8-mL teflon caped brown glass vials, GC vials and caps, micro GC vials.

2.4 Sample characterization

2.4.1 Sample pre-treatment

To assure sample stability and homogeneity, the sediment samples were sieved (< 2 mm), centrifuged to remove the supernatant, sediment texture and total organic content (TOC) were determined, then they were stored in glass jars at – 20 ^{o}C until analysis.

2.4.2 Moisture determination

The water content of the sediment samples was determined using oven method. 20-25 g of the sediment was dried overnight at 105 ^{o}C in the oven, then the sample was cooled in the desiccator and the difference in the sample weight was determined. Two trials for each sample were carried out and the average moisture content (H_2O %) was tabulated.

2.4.3 pH

The sediment pH value was determined by shaking 1:2.5 (w/w) ratio of sediment and distilled water, the mixture was homogenized for at least 15 min using horizontal shaker before the measurement with the pH-meter (Chapman, 1961).

2.4.4 Total organic carbon (TOC %)

The total organic carbon was determined by wet oxidation method and their results were confirmed using TOC analyzer method.

2.4.4.1 Wet oxidation method

Total organic carbon (TOC %) was determined according to Walkley-Black´s wet oxidation method (Baruah and Bathakur, 1997). 0.5-1.0 g of oven dried and fine-grained sediment, 10 mL of 1 N $K_2Cr_2O_7$ and 20 mL of concentrated sulfuric acid (H_2SO_4) were added. The mixture was gently shaken and allowed to stand for 30 min until completion of the oxidation reaction. The mixture was diluted with 200 mL of distilled water, then 10 mL of 85 % phosphoric acid (H_3PO_4) and 1.0 mL of diphenylamine indicator were added. Finally, the mixture was back titrated against 0.5 N ferrous sulfate ($Fe(NH_4)_2(SO_4)_2.6H_2O$), until violet color was observed. A blank titration was carried out in the similar manner, then TOC % was calculated according to the following formula:

$$TOC\ \% = (B-S)\times 0.5\times 0.003\times (100/W)\times 1.3\times 1.724$$

where

B : volume in mL of ferrous sulfate needed for blank titration,

S : volume in mL of ferrous sulfate needed for sample titration,

W : weight in grams of sample,

0.05 is normality of potassium dichromate, 0.003 is grams of organic carbon, 1.3 is Walkey correction factor and 1.724 is von Bemmlen factor.

2.4.4.2 TOC analyzer method

A well homogenized 2.0 g of oven-dry sediment sample was treated with 5-20 mL of 12.5 % HCl, until no more bubbling was observed. The excess amount of HCl was removed by heating using hot plate under fume hood, then the sample was filtered through simple filtration apparatus. To prevent the sample from hygroscopic characteristics which is gained after HCl treatment, the sample was washed with 20-30 mL of demineralized water and dried at 80 ^{o}C, then it was ground well again. 10 to 60 mg of the sample was analyzed, if the TOC content was high, a dilution factor of 10 times of the original sample was performed using alumina (Al_2O_3, ached at 800 ^{o}C). A

calibration curve ranged from 100 to 700 µg C was prepared using oxalic acid and alumina mixture ($H_2C_2O_4$ / Al_2O_3) in ratio of (1:9).

2.4.5 Sediment texture analysis

Sediment texture was determined using hydrometer method (Baruah and Bathakur, 1997). 50 g of oven-dry sediment was taken, in order to remove the organic matter, the sample was treated with 60 mL of 6 % H_2O_2 and heated over water bath at 80-90 ^oC. The process was repeated until frothing disappeared. The residual content was transferred to an 800 mL beaker and diluted with 400 mL distilled water, then 100 mL of Calgon reagent (5 % of sodium hexametaphosphate) was added. The suspension was stirred with help of magnetic stirrer for 15-20 min, then it was transferred into settling cylinder (1 L) which was sealed with Para-film and shaken for 1 min, the hydrometer was inserted immediately into the settling cylinder, and after 4 min, hydrometer reading (a) and suspension temperature were recorded. Finally, after 2 hours reading of hydrometer (b) and the suspension temperature recorded again. The hydrometer readings were corrected according to its calibration temperature. The particles size distribution were determined as follows:

Silt % = (a-b)/c×100

Clay % = (b/c) ×100

Sand % = 100-(Silt % + Clay %)

Where c is the weight in gram of the oven-dry sediment sample after subtraction of the weight of the oxidized organic matter.

Finally, the sediment texture was determined using the textural triangle.

2.5 Sample preparation

S19 multi-method was applied for the first sampling orientation period (Kolb et al., 1995). The applied part of the sample preparation is presented in **figure 2.6.**

2.5.1 Slurry extraction (S19 multi-method)

The wet homogenized sediment sample contained of 50 g of dry material was placed into 500 mL Erlenmeyer flask. Extraction was carried out with acetone/water mixture 2:1/v:v overnight using horizontal shaker at shaking velocity of 220 cycle/min. The liquid/liquid partitioning was performed by adding 15 g of NaCl and 100 mL cyclohexane, where the mixture was shaken for one hour. The organic layer was decanted into 250 mL Erlenmeyer flask and dried over 15 g sodium sulfate. 100 mL of

the extract were rotary evaporated and dissolved in 5 mL ethylacetate and cyclohexane mixture (1:1).

2.5.2 Gel permeation chromatography (GPC)

The sample was micro-filtered using PTFE syringe filter before GPC clean up. A 4 mL aliquot was injected into the GPC apparatus and the eluate was collected from 100 to 360 mL as the analyte fraction. The solution was rotary evaporated and concentrated to nearly dryness in a nitrogen stream, one drop of dodecane was used as a keeper, then the sample was dissolved in 1 mL of n-hexane.

2.5.3 Alumina column clean up

The alumina was activated overnight at 220 ^{o}C, then it was partly deactivated with 12.5 % H_2O and shaken for at least 4 hours using horizontal shaker. 10 g of deactivated alumina and 1.0 g of dried anhydrous Na_2SO_4 on the top of the chromatography column were used to separate non-polar from polar constituents of the sample matrix. The analyte was quantatively transferred to the alumina column and the non-polar fraction was eluted with 50 mL n-hexane, then it was rotary evaporated and concentrated to 1 mL. While, the polar fraction was eluted with 5 mL ethyl acetate followed by 100 mL of methanol/ammonia mixture 99:1 and rotary evaporated to 1 mL.

2.5.4 Silica gel column clean up

The silica gel was activated at 220 ^{o}C overnight, then it was partly deactivated with 2 % H_2O. The chromatographic column was packed with 10 g of deactivated silica gel and 1 g of oven dried anhydrous Na_2SO_4 on the top of the column. The non-polar fraction was transferred into the silica gel column and separated into three fractions: the first fraction was eluted with 50 mL n-hexane. The second fraction was eluted with 50 mL of n-hexane/ethyl acetate (49:1). Then, the third fraction was eluted with 50 mL ethyl acetate. Finally, each fraction which was collected during the silica clean up procedure was rotary evaporated and concentrated in a gentle nitrogen stream to 1 mL. 1,2,3,4-tetrachloronaphthalene (1,2,3,4-TCN) was used as internal standard for fractions 1 and 2. The sulfur was removed from the first fraction using tetrabutylammoniumsulfate method refer to section 2.6.2.4 (page 35). The first silica gel fraction was analyzed for PCBz, HCBz, and PCB congeners. However, the second and third fractions were analyzed for PAH and organochlorine compounds.

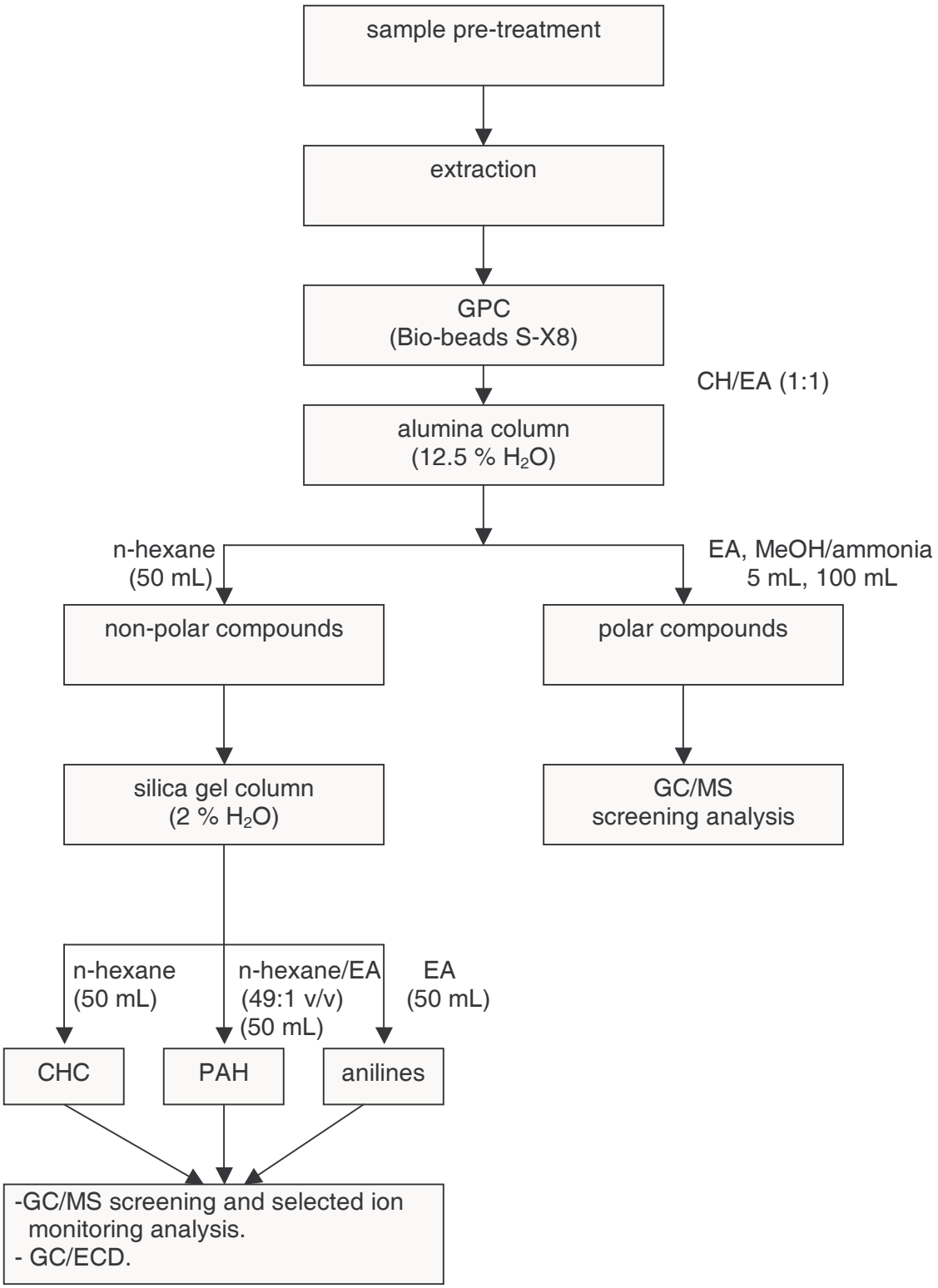


Figure 2.6. S19 multi-method, sample preparation scheme for the analysis of sediment and sewage sludge (Kolb et al., 1995).

2.6 Method development and optimization

The modified S19 analytical multi-method (Kolb et al., 1995) was not suitable for such sediment sample matrix, more details are discussed in section 3.1 (page 46). Therefore, a further modification on the analytical procedure was performed. The sample preparation scheme is presented in **figure 2.7**.

2.6.1 Extraction

Homogenized sediment sample containing 30 g of dry matter was used for extraction. The sediment sample was ground and mixed well with 70 g sea sand and 70 g anhydrous sodium sulfate using a 500-g porcelain mortar (Rossbach, 1992). The homogenized mixture was transferred into the extraction column which was rinsed 3 times with acetone and one time with n-hexane, then it was plugged with a piece of glass wool and 5 g of anhydrous sodium sulfate. The target compounds were extracted with 450 mL of n-hexane and acetone mixture (2:1) overnight. The flow rate was adjusted to 1 mL/min. The crude extract was rotary evaporated and concentrated near dryness in a gentle nitrogen stream and finally dissolved in 5 mL ethyl acetate/cyclohexane (1:1). The extract was filtered through a 0.47 mm PTFE syringe filter directly before GPC injection. Sample preparation and column extraction are exemplified in **figure 2.8**.

2.6.2 Clean up

Sophisticated clean up procedure was developed to enhance the quality of the chromatographic analysis, because most of the co-extractants and the instrumental interfering materials were removed.

2.6.2.1 Gel permeation chromatography (GPC)

A 4 mL aliquot was injected into the GPC apparatus and the eluate was collected from 110 to 380 mL as the analyte fraction. This time was increased to ensure that all PAH were eluted. The solution was rotary evaporated and concentrated to nearly dryness in a nitrogen stream, then it was dissolved in 1.0 mL n-hexane. Appearance of precipitate at this step was observed for most of sample analytes.

2.6.2.2 Alumina column clean up

The alumina was activated at 220 ^{o}C overnight, then it was deactivated with 12.5 % H_2O and shaken for at least 4 hours using horizontal shaker (220 cycle/min) to get

homogenous deactivation directly before use. 10 g of partly deactivated neutral alumina and 1 g of dried anhydrous Na_2SO_4 on the top of the chromatography column were used to separate non-polar from polar constituents of the sample matrix. The analyte was quantitatively transferred to the alumina column and the non-polar fraction was eluted with 60 mL n-hexane. Then it was rotary evaporated and concentrated to 1 mL.

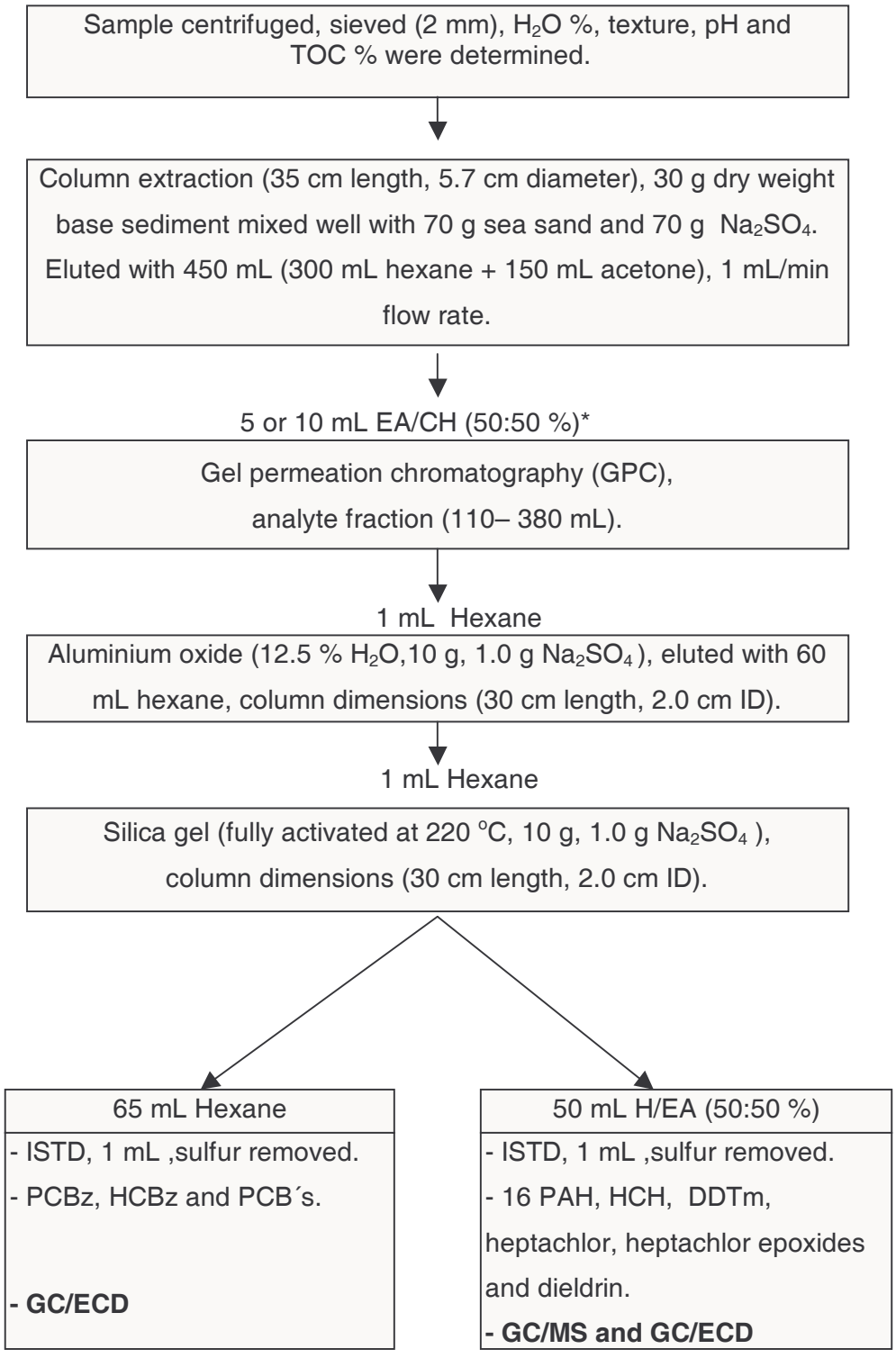
2.6.2.3 Silica gel column clean up

In order to eliminate most of interfering substances in the instrumental analysis, further clean up procedures were aimed at separating target compounds into two fractions. The silica gel was activated at 220 ^{o}C overnight before use. The chromatographic column was packed with 10 g of fully activated silica gel and 1 g of oven dried anhydrous Na_2SO_4 on the top of the column. After introducing the analytes into the silica gel column two fractions were collected: the first fraction was eluted with 65 mL n-hexane, which was further analyzed for PCBz, HCBz, and PCB congeners. The second fraction was eluted with 50 mL of ethyl acetate/n-hexane (1:1) and analyzed for PAH and organochlorine pesticides.

Finally, 50 µL dodecane was added as a keeper and each fraction was rotary evaporated and concentrated in a gentle nitrogen stream. 1,2,3,4-tetrachloronaphthalene (1,2,3,4-TCN) was used as internal standard and added before bringing the final volume to 1 mL.

2.6.2.4 Sulfur removal

Before instrumental analysis, the elemental sulfur was removed from both silica gel fractions using tetra butyl ammonium sulfite (TBAS) method (Jensen et al., 1977). Into a teflon screw cap test tube which was rinsed with acetone and n-hexane, 1 mL of 0.1 M TBAS reagent (0.68 g TBAS and 5.0 g Na_2SO_3, dissolved in 20 mL Milli-Q water) mixed with 1.0 mL isopropanol and few crystals of sodium sulfite, then the sample was transferred quantitatively into the same test tube, the mixture was shaken for 1 min. The phase separation was carried out by adding 2.5 mL Milli-Q water and then shaken for 1 min, few crystals of sodium sulfite were added until appearance of a white precipitate. Finally, the clear upper n-hexane layer was collected and transferred into a GC vial.



*EA: ethyl acetate, H: n-hexane, CH: cyclohexane.

Figure 2.7. Modified sample preparation scheme.

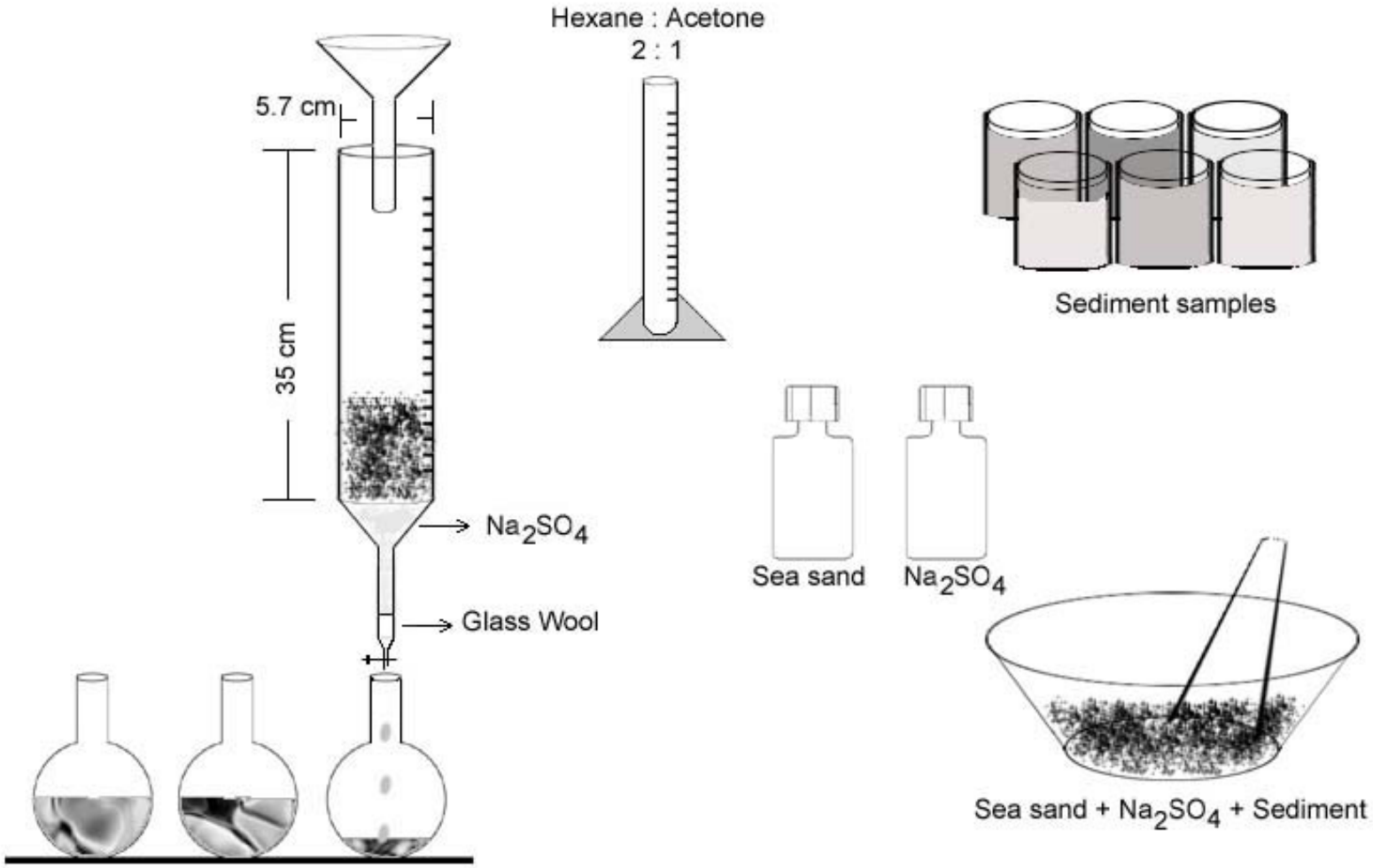


Figure 2.8. Sample preparation and column extraction.

2.7 Chromatographic sample analysis

The non-target compound analysis was performed as preliminary sample constituents identification using gas chromatography coupled to mass selective detector (GC/MS) which was operated in full scan mode. Later on, target compounds analysis was carried out for PCBz, HCBz, PCB, and organochlorine pesticides using gas chromatography coupled to electron capture detector (GC/ECD) and PAH using GC/MS .

2.7.1 Standards and calibration

Calibrations of organochlorine compounds were performed by internal standardization at two working calibration levels: the first calibration level ranged 10-100 pg/µL, and the second calibration level ranged 100-1000 pg/µL. The concentration of internal standard was remained constant at 1000 pg/µL. The chromatographic peak areas were fitted by linear regression and the correlation coefficients (R^2) exceeding 0.995 were accepted.

For US-EPA 16 PAH external standardization was carried out at a calibration level of 100-3000 pg/µL using matrix standards. When it was necessary, the samples were diluted 10 times to meet the calibration range. The correlation coefficients for the calibration curves exceeded 0.998. Finally, quality assurance measurements were carried out performing fortification experiments for all target compounds. In addition, the precision of the analytical procedures was expressed as relative standard deviation (RSD), where 20 % as RSD was the maximum acceptable value. This concept was controlled by numerous repetitions of the analysis for each sampling campaign. More concepts are discussed in details in the quality assurance section.

2.7.2 Analysis of organochlorine compounds

A Hewlett-Packard 5890 Series II GC chromatograph equipped with HP 6890 Series injector and coupled to a ^{63}Ni electron capture detector was used for analysis of PCBz, HCBz, PCB 28, PCB 52, PCB 101, PCB 138, PCB 180, α-, β-, γ-, and δ-hexachlorocyclohexane isomers, o,p-DDE, p,p´-DDE, o,p-DDD, p,p´-DDD, heptachlor, cis-heptachloro epoxide, trans-heptachloro epoxide, and dieldrin. A 1 ng/µL of 1,2,3,4-tetrachloronaphthalene was used as internal standard and it was added directly before the chromatographic injection. A 1.0 µL aliquot was injected into DB-5 fused silica capillary column with 60 m length, 0.25 µm film thickness and 0.32 mm inner diameter

(J&W Scientific, USA). Helium was used as carrier gas and nitrogen as make up gas, the carrier gas flow rate was 2 mL/min and the total flow 60 mL/min. The Hewlett-Packard Chem Station was used for data analysis and management. The results were confirmed using the same instrument, but coupled to DB-1701 fused silica capillary column. GC-ECD instrument operation conditions are presented in **table 2.4**.

Table 2.4. Instrument operation conditions for GC/ECD.

Target compounds	Type of capillary column	Temperature program and other conditions[#]
PCBz, HCBz, and PCB	DB-5 (60 m×0.25 µm×0.32 mm i.d.)	60 °C (1 min) to 160 °C (1 min) at rate 15 °C/min, then to 220 °C (5 min) at 5 °C/min, finally at 3 °C/min to 280 °C (15 min).
	DB-1701 (45 m×1.0 µm×0.32 mm i.d.)	80 °C to 160 °C at rate 30 °C/min, then to 220 °C at 10 °C/min, finally at 5 °C/min to 280 °C (30 min).
Organochlorine pesticides	DB-5 (60 m×0.25 µm×0.32 mm i.d.)	60 °C (5 min) to 160 °C (3 min) at rate 10 °C/min, then to 220 °C at 2 °C/min, finally to 280 °C (15 min) at rate 8 °C/min.
	DB-1701 (45 m×1.0 µm×0.32 mm i.d.)	80 °C to 220 °C (20 min) at rate 30 °C/min, then to 280 °C (15 min) at ramping rate 2 °C/min.

Note: the injector and detector temperatures were remained constant at 250 °C and 300 °C, respectively. Helium was used as carrier gas with flow rate 2 mL/min. The injection volume was 1 µL splitless.

2.7.3 Analysis of PAH

GC/MS determination was performed using a Hewlett-Packard HP 5890 Series II gas chromatograph equipped with HP 7673 KAS programmable auto injector operated at 80 ^{o}C to 350 ^{o}C at a rate of 13.5 ^{o}C/s. The gas chromatograph was coupled to an HP 5970 Series mass selective detector (MSD) with electron ionization mode (EI ionization). The mass spectrometer was operated in full scan mode as well as in selected ion monitoring mode (SIM) detecting the M^{+} ions for 16 PAH and the ionization source was supplied with voltage at 70 eV. A 1 µL of aliquot was injected into the KAS injector. A DB-5 MS fused silica capillary column with 30 m length, 0.25 µm film thickness and 0.25 mm inner diameter was used (J&W Scientific, USA). The oven temperature program was 60 ^{o}C (4 min) ramped at 15 ^{o}C/min to 160 ^{o}C, then at 3 ^{o}C/min to 280 ^{o}C, finally hold for 10 minutes. The transfer line temperature was maintained at 280 ^{o}C and the carrier gas (He) flow rate was 1 mL/min.

2.7.4 GC/MS full scan

The same GC/MS was used for preliminary identification of the sample matrix as well as the relevant environmental organic pollutants for the first sampling period using full scan monitoring mode. The collected mass spectra were searched using MS Wiley spectrum library.

2.7.5 GC/MS SIM program for PAH

Specific mass to charge ratios (m/z) were used for selected ion monitoring program for the 16 PAH. These ratios are summarized according to the chromatographic elution in **table 2.5**.

2.8 Chromatographic detection problems

The main important chromatographic problems were the presence of elemental sulfur in the sediment samples and the sample co-extractants. These two problems are discussed in the following section.

Table 2.5. Selected ion monitoring (SIM) program for 16 US-EPA PAH.

No.	Target compound	Abbreviation	m/z
1	Naphthalene	NAP	128
2	Acenaphthylene	ACY	152
3	Acenaphthene	ACE	154
4	Fluorene	FLE	166
5	Phenanthrene	PHE	178
6	Anthracene	ANT	178
7	Fluoranthene	FLA	202
8	Pyrene	PYR	202
9	Benzo[a]anthracene	BaA	228
10	Chrysene	CHR	228
11	Benzo[b]fluoranthene	BbF	252
12	Benzo[k]fluoranthene	BkF	252
13	Benzo[a]pyrene	BaP	252
14	Indeno[1,2,3,4,cd]pyrene	IcdP	276
15	Dibenzo[a,h]anthracene	DahA	278
16	Benzo[g,h,i]perylene	BghiP	276

2.8.1 Effect of sulfur on GC/ECD

In GC/ECD analysis, elemental sulfur interferes with separation of organochlorine compounds, it saturates the electron capture detector and produces high baseline. Detection of the organochlorine compounds was not possible in the presence of the elemental sulfur which occurs mainly into the first silica gel fraction. It was removed using tetrabutylammoniumsulfite (TBA) method (Jensen, 1977), which converts the solid sulfur from the organic phase into aqueous phase as soluble thiosulfate according to the following reaction: $(TBA^{+})_2SO_3^{2-}+S(s) \longrightarrow 2TBA^{+}+S_2O_3^{2-}$. Effect of sulfur on electron capture detector (ECD) is represented in **figure 2.9**, and after sulfur removal in **figure 2.10** for the same sample. Note the different scales of the y-axis for both figures.

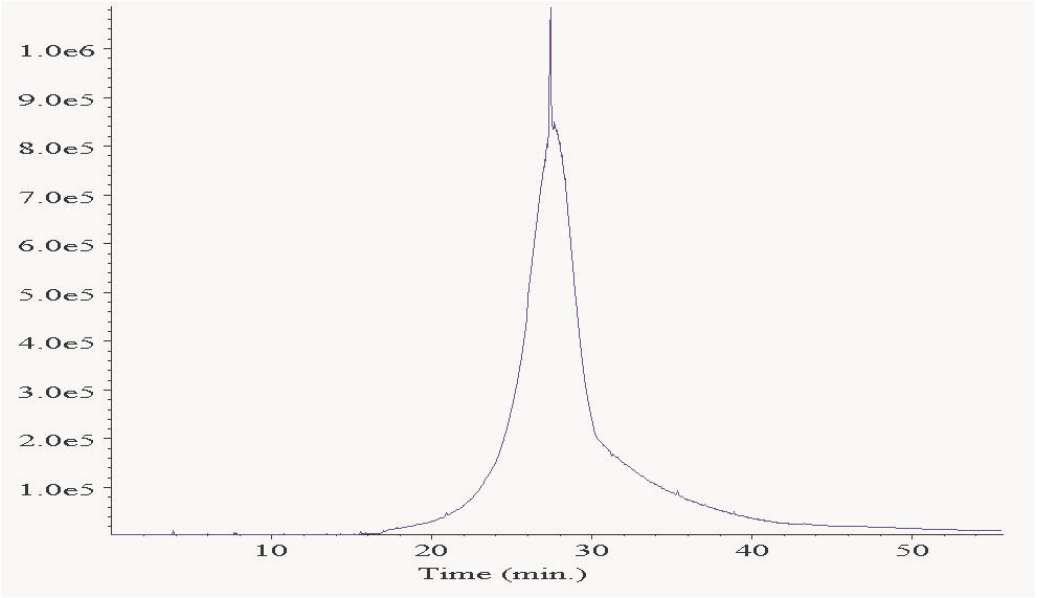


Figure 2.9. GC/ECD chromatogram in presence of sulfur.

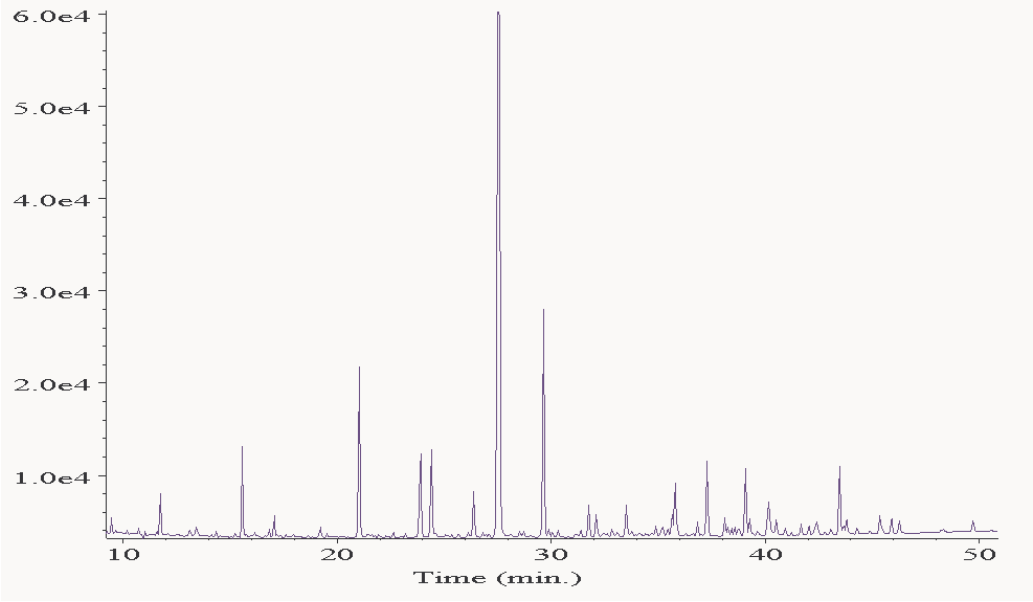


Figure 2.10. GC/ECD chromatogram after sulfur removal.

2.8.2 Sample matrix effect

The sediment sample extract is characterized usually by complex matrix. Most of the co-extractants were removed during clean up procedure. Nevertheless, the sample matrix for the second silica gel fraction still contained interferences and co-elutants. **Figures 2.11** and **2.12** show the effect of the sample matrix variability for second silica gel fractions.

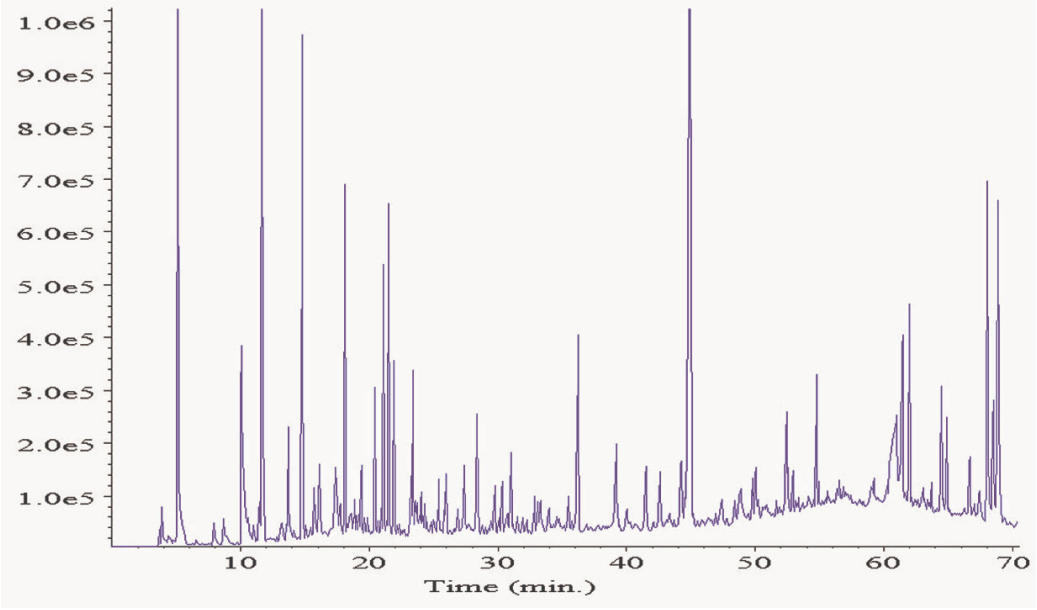


Figure 2.11. GC/ECD chromatogram presents the sample matrix effect for second silica gel fraction (site: AD3).

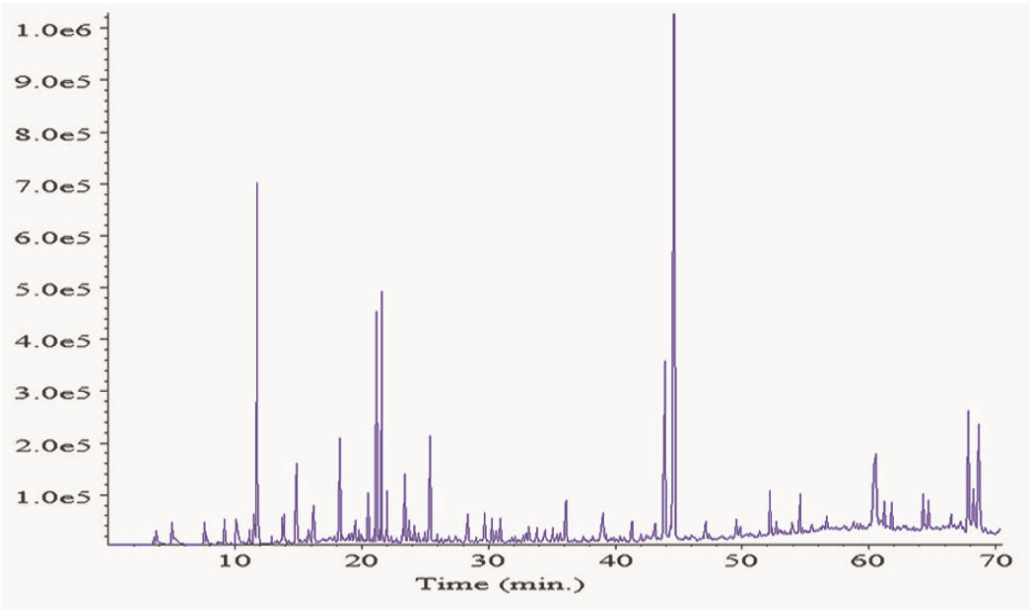


Figure 2.12. GC/ECD chromatogram presents less effect of the sample matrix for second silica gel fraction (site: R1).

2.9 Quality assurance

The quality assurance measures were divided into five parts: firstly limit of determination (LOD) of the analytical method, secondly detection limit (DL) and instrument detection limit (IDL), thirdly precision of the modified method, fourthly

confirmation of the analytical results and finally quality assurance of the sampling storage and ageing.

Fortification experiments were performed for all target compounds in order to determine the limit of determination. 10 g of sediment samples (n=4) were spiked with: 12.5 µg/kg of 16 PAH standard, 1.25 µg/kg of PCBz, HCBz, and 6 PCB congeners, and finally with 2.5 µg/kg of 12 different organochlorine pesticides. One sediment sample was left unspiked and processed as a blank due to the absence of zero-sediment sample (free from target compounds), then the spiked as well as unspiked samples were subjected to the analytical procedure. Later on the detected concentrations of the target compound were obtained in the blank sample and subtracted from the spiked concentrations for the fortified samples in order to determine the recovery rates.

The detection limit and the instrument detection limit for organochlorine compounds were calculated based on signal to noise ratio (3:1) for sample and standard matrixes, respectively. Average of 10 GC/ECD sample chromatograms were calculated for their average noise to signal ratios, and the linearity ($R^2 > 0.995$) of the calibration standards was taken in consideration in case of instrument detection limit. However, the GC/MS detection limit was obtained based on linearity of lowest PAH standards calibration, where R^2 has exceeded 0.998. The precision or repeatability of the analytical method was expressed as relative standard deviation (RSD) and its acceptable value was below 20 %. The number of samples analysed for repeatability purposes were 5 replicates for summer season and 3 replicates for winter season. In addition, most of the samples which have shown extreme results such as WZ1 were analysed in two or three replicates and average values were tabulated.

Confirmation of GC/ECD results was performed using two column technique. The analytical results which were collected using low polar DB-5 capillary column were confirmed using medium polarity DB-1701capillary column. The specification and the analytical operating conditions for both used columns are presented in **table 2.4**. However, GC/MS results does not need any confirmation because in addition to the retention time the mass spectrum of each PAH was available using selected ion monitoring GC/MS analysis.

The wet oxidation results for total organic carbon was confirmed using infrared CO_2-analyzer method. Effect of biological activity which might be taken place during sample

storage and ageing was controlled by analyzing same samples for their organic pollutants content after 8-11 month storage time.

2.10 Physical and chemical properties of sediments

The determined physical and chemical properties of the sediments samples pH, H_2O % and total organic matter (TOC %) are summarized in **table 2.6** for summer and winter seasons.

Table 2.6. Physical and chemical sediments properties for summer and winter sampling periods

Site	pH	TOC [%]	H_2O [%]	Site	pH	TOC [%]	H_2O [%]
Z1	7.46	2.45	18.65	**WZ1**	6.23	13.00	52.46
Z2	7.12	8.41	26.38	**WZ2**	7.22	3.84	24.31
Z3	7.04	7.31	26.63	**WZ3**	7.07	4.90	29.90
Z4	6.69	11.34	30.42	**WZ4**	7.51	2.85	24.12
Z5	6.74	10.95	33.95	**WZ5**	7.95	0.75	20.73
Z6	6.90	5.37	28.63	**WZ6**	7.49	7.61	39.92
Z7	7.17	5.60	27.98	**WZ7**	7.57	0.67	21.15
Z8	7.54	4.23	25.66	**WZ8**	7.37	3.83	25.18
Z9	7.34	2.41	25.10	**WZ9**	7.33	5.34	23.93
Z10	7.59	2.81	22.75	**WZ10**	7.42	2.26	20.87
D1	7.17	19.46	61.26	**WD1**	8.14	2.79	23.53
D2	6.36	28.09	52.52	**WD2**	7.56	4.97	39.08
BD3	6.76	25.58	45.32	**WBD3**	7.39	5.96	39.48
D3	7.11	14.88	43.39	**WD3**	7.28	34.68	70.53
AD3	6.90	23.69	49.03	**WAD3**	7.49	17.01	59.68
FD3	7.08	17.33	36.92	**WFD3**	7.18	6.82	49.45
D4	7.25	4.34	27.19	**WD4**	7.40	3.06	24.62
R1	7.12	5.81	26.10	**WR1**	7.82	1.82	20.93
R2	7.73	1.43	18.00	**WR2**	7.62	1.96	21.50
R3	7.32	5.05	30.31	**WR3**	8.01	1.95	23.01
				WR4	7.93	1.63	26.03
				Ref.site	8.21	1.89	22.68
				I.waste	-	97.49	84.11

* pH:- Sediments to water ratio (1:2.5) and shaken for 15 min before measurement.
** n.a:- not analysed.

3. Results and discussion

Totally, all sediment samples were collected in the periods of December 2000, and from November 2001 to January 2002. They were characterized for total organic carbon, particle size distribution and pH value. In addition, they were analyzed for 16 PAH, 6 PCB congeners, PCBz, HCBz and 12 organochlorine pesticides using the modified analytical method. The mobility and bioavailability of organic contaminants which are associated with sediment beds depend on the concentrations of these compounds in the porewater (Bahadir et al., 1992; Mcgroddy et al., 1996). The hydrophobic organic compounds are adsorbed to sediment particles as a result of their partitioning between porewater and sediment organic matter (Kile et al., 1995; Kukkonen and Landrum, 1996; Pingnatello and Xing, 1996). The modification of the analytical method and the results of quality assurance measurements are discussed in detail below.

3.1 Modification of the analytical method

In the preliminary orientation phase of the present work the modified S19 analytical multi-method (Kolb et al., 1995) was applied for the first sample preparation and analysis. However, it was not suitable for such sediment sample matrix, where the first problem has appeared during the extraction procedure using a mixture of acetone and water (2:1). However, liquid/liquid partitioning was not successfully performed using cyclohexane (emulsion was formed). That might be explained as an ionic surfactants effect which can be aggregated on the sediment beds to form a pseudophases (Edwards et al., 1994). Therefore, switching from slurry extraction to column extraction procedure was performed. The goals were to reduce the surfactants effect using anhydrous sodium sulfate which adsorbed the sediment moisture, and to eliminate water from the extraction procedure.

Environmental analysis often include a determination of anionic surfactants when assessing surface water pollution. Industrial facilities can discharge anionic detergents into the water supply, soap manufacturers also, and other sources are household cleaners and personal care products (Ding et al., 1999). The Colorimetric Method methylene blue active substances (MBAS) is used to measure anionic surfactants and the results are expressed in mg/L as linear alkylbenzene sulfonate (LAS) (EPA, 1983). Industries as well as wastewater treatment plants which are located along Zarqa River

contaminate the aquatic sediments with huge amount of anionic surfactants. The quality of As-Samra effluents which flow into Zarqa River is presented in **figure 3.1**, where a big amount of foam “desert snow” is formed because of its high surfactants content. The efficiency of As-Samra WSPs to remove these industrial surfactants dose not exceeded 35 % (Anonymous, 2000c). Furthermore, the quality of the industrial effluents for some selected industries are summarized in **table 1.3** (page 14), where MBAS value ranged from 0.2-1800 mg/L for certain industrial effluents. However, the maximum allowable amount of surfactants in industrial effluents is 25 mg/L according to the Jordanian industrial wastewater standards (JIWS) (Anonymous, 2000c).

Figure 3.1. Quality of As-Samra effluents which flow into Wadi Dhuleil.

3.2 Quality assurance

The quality assurance procedures can be defined as a number of measurements that should be performed to ensure a sufficient quality of the analysis (Kleiböhmer, 2001).

3.2.1 Instruments detection limit (IDL)

Controlling the performance of the analytical instrument is one of the good laboratory practices that leads to produce stable and precise results. Therefore, IDL was controlled for GC/ECD based on the linearity of calibration curves and the signal to noise ratio (3:1) for standard solutions. However, for GC/MS only the linearity of the

calibration curves was controlled. The IDL for GC/ECD was 3 to 4 times more sensitive than the detection limit and limit of determination. However, GC/MS was more sensitive by 24 to 96 times higher than the limit of determination for PAH. The instruments detection limits (IDL) for the target compounds are shown in **table 3.1**.

Table 3.1. Instruments detection limits in pg/μL for GC/ECD and GC/MS.

Analyte	GC-ECD	Analyte	GC/MS
PCBz	1.00	o,p´-DDD	2.25
HCBz	0.50	p,p´-DDD	2.10
PCB 28	1.00	naphthalene	5.00
PCB 52	2.00	acenaphtylene	2.50
PCB 101	1.00	acenaphtene	2.50
PCB 138	2.00	fluorene	2.50
PCB 153	2.00	phenanthrene	2.50
PCB 180	0.50	anthracene	5.00
α-HCH	2.00	fluoranthene	5.00
β-HCH	2.00	pyrene	5.00
γ-HCH	2.00	benzo[a]anthracene	10.00
δ-HCH	2.00	chrysen	10.00
heptachlor	4.25	benzo[b]fluoranthene	10.00
cis-heptachlor epoxide	1.74	benzo[k]flouranthene	10.00
trans-heptachlor epoxide	2.00	benzo[a]pyrene	7.50
dieldrin	3.25	indeno[1,2,3,4,c,d]pyrene	7.50
o,p´-DDE	2.25	dibenzo[a,h]anthracene	7.50
p,p´-DDE	2.75	benzo[g,h,i]perylene	7.50

3.2.2 Limits of determination (LOD)

The levels at which detection becomes problematic is defined as limits of determination (LOD) of that analytical method (Ellison et al., 2000). The LOD was determined by performing fortification experiment for all target compounds in order to control the extraction and clean up procedure. Generally, good recovery rates ranged over 70-110 % with RSD less than 20 %. The recoveries rates were determined for each analyte based on blank-correction. The analytical results have appeared good recoveries for all target compounds, except low recoveries were obtained for PCBz and naphthalene because of their high volatility, whereas, β-HCH has shown high “recovery rate” due to matrix interferences. Recovery findings and limit of determination for all target compounds are presented in **table 3.2**.

Table 3.2. Recovery rate and limit of determination (LOD) of target compounds (LOD was calculated for 10 g of dry weight sediment, n = 4).

Target compound	Fortification level [µg/kg]	Recovery rate [%]				LOD [µg/kg]
		Minimum	Maximum	Average	SD	
16 PAH						
naphthalene	12.50	59	65	62	2.5	10.0
acenaphtylene	12.50	69	72	70	1.3	10.0
acenaphtene	12.50	71	75	73	1.7	10.0
fluorene	12.50	80	81	80	0.5	10.0
phenanthrene	12.50	80	93	84	6.1	10.0
anthracene	12.50	89	92	90	1.4	10.0
fluoranthene	12.50	87	105	96	7.4	10.0
pyrene	12.50	85	93	93	6.5	10.0
benzo[a]anthracene	12.50	84	101	93	6.9	10.0
chrysene	12.50	89	106	98	6.9	10.0
benzo[b]fluoranthene	12.50	88	108	98	8.2	10.0
benzo[k]flouranthene	12.50	90	106	98	6.5	10.0
benzo[a]pyrene	12.50	79	98	89	7.8	10.0
indeno[1,2,3,4,cd]pyrene	12.50	80	106	89	12.0	10.0
dibenzo[a,h]anthracene	12.50	76	101	88	10.2	10.0
benzo[g,h,i]perylene	12.50	78	104	91	10.6	10.0
Organochlorine compounds						
pentachlorobenzene	1.25	52	59	56	2.9	1.0
hexachlorobenzene	1.25	70	81	76	4.6	1.0
PCB 28	1.25	74	94	88	9.9	1.0
PCB 52	1.25	78	112	95	13.9	1.0
PCB 101	1.25	97	132	109	16.1	1.0
PCB 138	1.25	77	86	81	3.7	1.0
PCB 153	1.25	91	106	98	6.1	1.0
PCB 180	1.25	95	116	106	8.6	1.0
α-HCH	2.50	90	106	95	7.5	2.0
β-HCH	2.50	118	203	159	34.8	2.0
γ-HCH	2.50	88	102	95	5.7	2.0
δ-HCH	2.50	87	97	91	4.5	2.0
heptachlor	2.50	92	126	108	13.9	2.0
cis-heptachlor epoxide	2.50	107	115	110	3.4	2.0
trans-heptachlor epoxide	2.50	92	101	96	3.7	2.0
dieldrin	2.50	95	105	99	4.2	2.0
o,p´-DDE	2.50	104	108	106	1.7	2.0
p,p´-DDE	2.50	105	108	106	1.3	2.0
o,p´-DDD	2.50	94	127	112	13.7	2.0
p,p´-DDD	2.50	108	127	115	8.5	2.0

3.2.3 Detection limit (DL)

The lower concentration of the practical operating range of a method is defined as detection limit (DL) (Ellison et al., 2000). The DL was determined by comparing the signal to noise ratio (3:1) for the samples matrices. However, DL values were found close or much lower compared to LOD. It was noticed that the DL and LOD are highly dependent on the sample matrix, especially for the second fraction of silica gel column, which was characterized by complex sample matrix that contained most of the co-extractants. Therefore, detection limit has shown high variability for the organochlorine pesticides, while lower variability obtained for PCBz, HCBz, and PCB for the first silica gel fraction. The detection limits for PCBz, HCBz, PCB, and organochlorine pesticides expressed as µg/kg of dry weight and based on signal to noise ratio (3:1) are presented in **table 3.3**.

Table 3.3. Detection limits (DL) [µg/kg d.w.] for PCBz, HCBz, PCB congeners, and organochlorine pesticides were determined using GC/ECD coupled to DB-5 capillary column and based on signal to noise ratio (3:1) for the sample matrix.

Analyte	Minimum	Maximum	Average	SD (n=6)
PCBz	0.08	0.11	0.10	0.01
HCBz	0.05	0.09	0.07	0.02
PCB 28	0.10	0.18	0.15	0.03
PCB 52	0.09	0.14	0.12	0.02
PCB 101	0.10	0.17	0.14	0.03
PCB 138	0.10	0.17	0.14	0.02
PCB 153	0.11	0.16	0.14	0.02
PCB 180	0.10	0.16	0.14	0.02
α-HCH	0.33	1.28	0.84	0.32
β-HCH	0.38	1.70	1.09	0.47
γ-HCH	0.33	2.16	1.07	0.62
δ-HCH	0.37	1.44	0.98	0.38
heptachlor	0.53	2.08	1.17	0.56
cis-heptachlor epoxide	0.40	1.57	1.06	0.41
trans-heptachlor epoxide	0.39	1.53	0.99	0.37
dieldrin	0.59	2.30	1.39	0.56
o,p´-DDE	0.57	2.24	1.35	0.55
p,p´-DDE	0.92	3.58	2.24	0.86
o,p´-DDD	0.75	2.93	1.84	0.70
p,p´-DDD	0.84	3.26	2.15	0.81

3.2.4 Fortification experiments

Fortification experiments were performed for all target compounds in order to control the extraction and clean up procedures as well as the GC analysis. The percent for each analyte was determined by comparing the blank-corrected and measured concentrations with the spiked concentrations. The recovery rates for PAH ranged from 62 to 98 % (**figure 3.2**), and recoveries of organochlorine compounds ranged from 56 to 159 % (**figure 3.3**). Generally, the developed method has shown an acceptable recovery rate for most of the target compounds. However, low recoveries were obtained for naphthalene and PCBz, except high "recovery rate" observed for β-HCH.

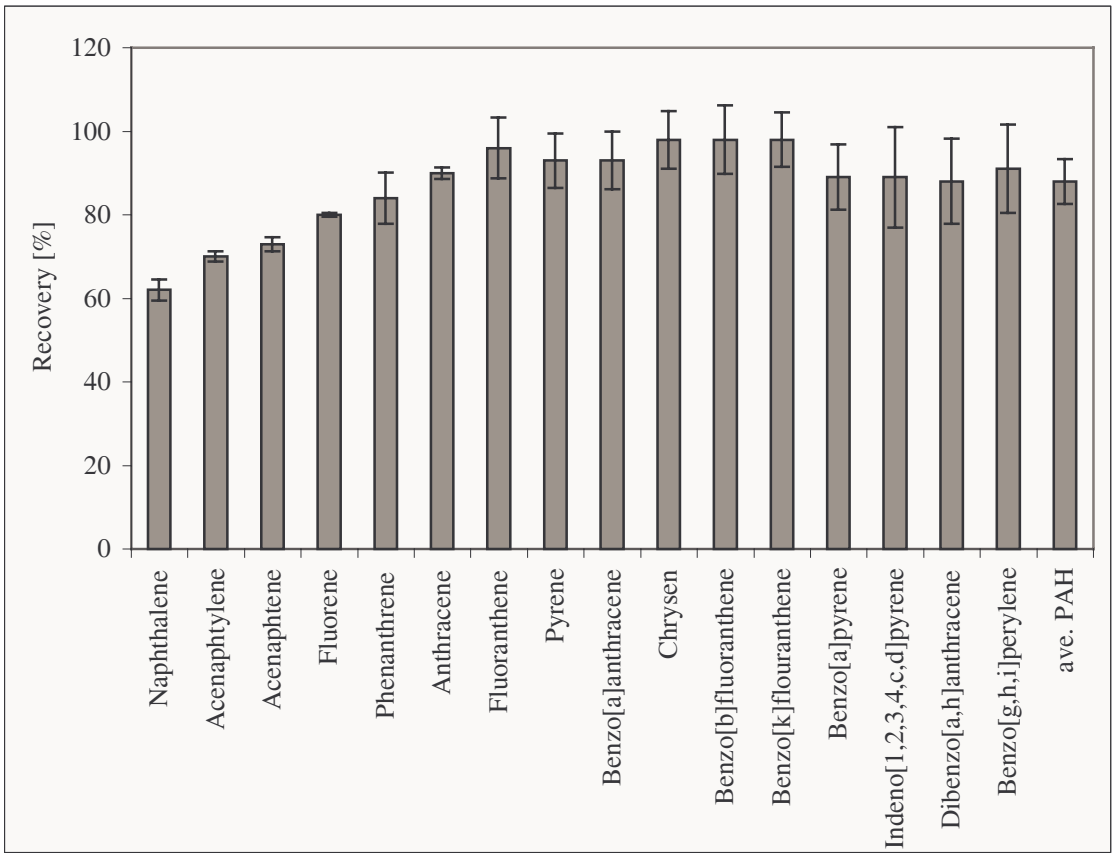


Figure 3.2. Recovery rates of 16 US EPA-PAH.

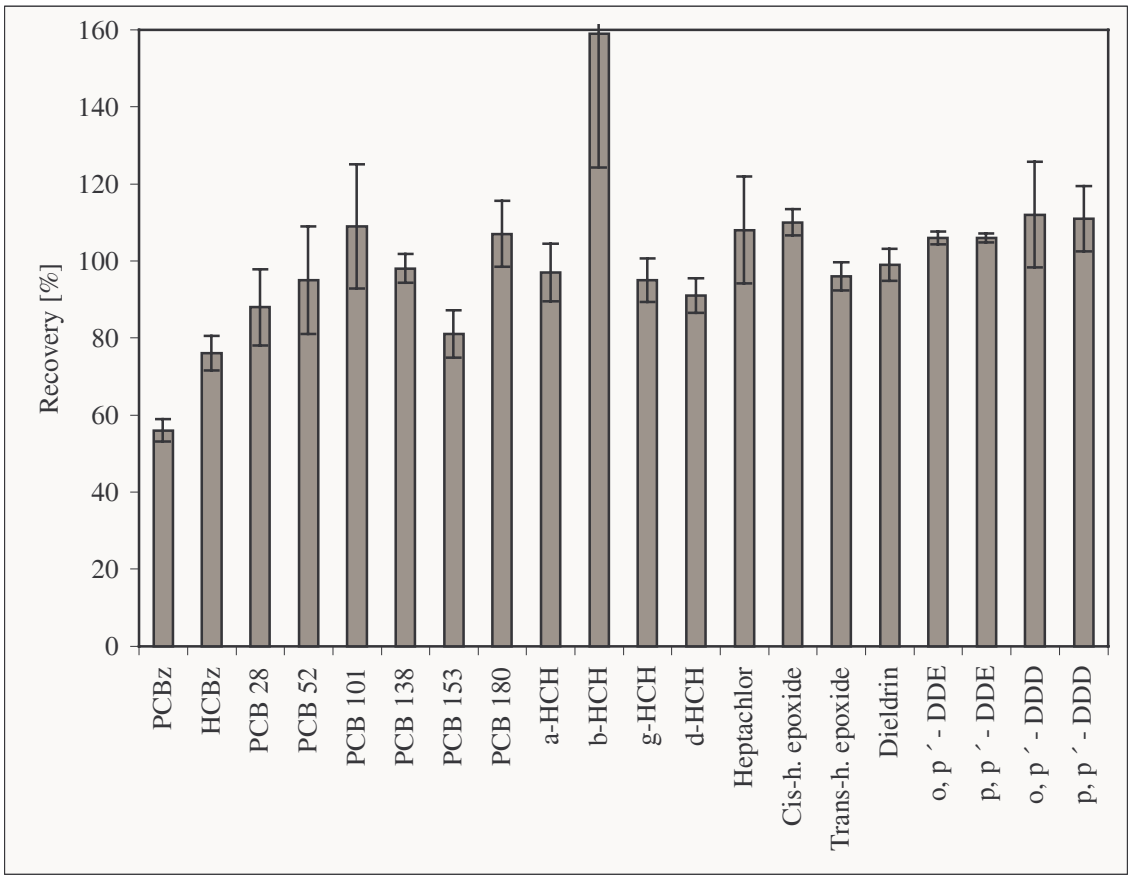


Figure 3.3. Recovery rates of organochlorine compounds.

3.2.5 Repeatability

The analytical repeatability of the results are expressed as relative standard deviation (RSD), and it represents the precision of the analytical procedure. The number of samples analysed for repeatability purposes are 5 replicates for summer season and 3 replicates for winter season. In addition, most of the samples which have shown extreme results were analysed in two or three replicates and average values were tabulated. The precision of the analytical method is summarized as RSD in **table 3.4** for all target compounds for both sampling periods and more details are presented in the **appendix**. Further details of the repeatability findings are discussed in the following sections.

3.2.5.1 PAH

The analytical repeatability was generally acceptable for 16 PAH, mostly the RSD was less than 10 %, except that for naphthalene in summer season (RSD = 34.6) which might be explained as losses during sample preparation due to its high volatility. The

analytical repeatability results are presented in **tables 7** and **8** in the **appendix** for summer and winter seasons, respectively.

Table 3.4. Precision of the analytical method presented as RSD for all target compounds and for both sampling periods.

Target compound	Summer RSD (n=5)	Winter RSD (n=3)	Target compound	Summer RSD (n=5)	Winter RSD (n=3)
PCBz	14.5	ND	naphthalene	34.6	1.7
HCBz	9.7	28.4	acenaphtylene	3.7	1.9
PCB 28	54.9	33.4	acenaphtene	8.2	1.5
PCB 52	38.8	4.9	fluorene	8.1	3.6
PCB 101	10.7	22.2	phenanthrene	9.1	3.4
PCB 138	8.6	8.4	anthracene	7.3	2.9
PCB 153	17.3	14.1	fluoranthene	8.4	3.2
PCB 180	8.4	8.13	pyrene	10.0	2.3
α-HCH	14.3	11.1	benzo[a]anthracene	6.0	4.2
β-HCH	ND	28.1	chrysene	10.2	4.9
γ-HCH	ND	ND	benzo[b]fluoranthene	7.9	7.4
δ-HCH	ND	45.6	benzo[k]flouranthene	5.9	5.7
heptachlor	ND	40.5	benzo[a]pyrene	7.7	10.2
cis-heptachlor epoxide	9.2	ND	indo[1,2,3,4,c,d]pyrene	4.4	ND
trans-heptachlor epoxide	10.0	ND	dibenzo[a,h]anthracene	6.3	ND
dieldrin	ND	8.1	benzo[g,h,i]perylene	8.1	ND
o,p´-DDE	19.5	2.4	ΣPAH	6.5	2.8
p,p´-DDE	5.9	10.7	ΣPCB	13.1	22.2
o,p´-DDD	7.3	6.5	ΣDDTm	7.9	5.6
p,p´-DDD	3.9	2.1			

3.2.5.2 PCBz, HCBz, and PCB

This group of analytes is found in the first silica gel fraction and the analytical repeatability findings are presented in **tables 9** and **10** in the **appendix** for summer and winter seasons, respectively. The relative standard deviations for all analytes were less than 20 %, except those for PCB 28 and PCB 52 which have shown high RSD values, that might be explained as a consequence of their partition during silica gel clean up

procedure as well as due to co-eluting problems, for instance PCB 28 is co-eluted with PCB 31.

3.2.5.3 Organochlorine pesticides

Organochlorine pesticides were found in the second fraction of silica gel column which contained most of the co-extractants. However, a good precision of the analytical procedures were obtained for most of organochlorine pesticides which expressed as RSD (< 20 %), except that for β-HCH, δ-HCH, and heptachlor in winter season and that might be explained due to the co-eluting problems appeared from sample matrix interferences. In addition, high RSD have been obtained for some of these analytes which were detected in lower concentrations than detection limits. The analytical repeatability findings are listed in **tables 11** and **12** in the **appendix** for both sampling periods.

3.2.6 Confirmation of GC/ECD results

Two column technique was used for confirmation of GC/ECD results. The analytical results were recorded using low polarity DB-5 fused silica capillary column and confirmed using medium polarity capillary column DB-1701. For confirmation purpose, selected samples were analyzed and a part of the results are presented in **table 3.5** for CBz and PCB.

Table 3.5. Example for part of GC/ECD confirmation results obtained using DB-5 and DB-1701 columns, concentration presented as [µg/kg d.w.].

sample	Z4		Z5		BD3	
column	DB-5	DB-1701	DB-5	DB-1701	DB-5	DB-1701
analyte						
PCBz	<DL	<DL	<DL	<DL	<DL	<DL
HCBz	3.3	3.5	1.5	1.7	1.0	0.7
PCB 28	2.4	1.4	1.3	1.8	3.4	1.8
PCB 52	0.8	<DL	<DL	<DL	2.2	<DL
PCB 101	0.8	0.9	0.6	0.7	0.4	0.5
PCB 153	1.4	1.7	1.5	1.5	1.4	1.8
PCB 138	1.3	2.0	1.3	1.7	1.2	1.2
PCB 180	1.0	1.1	1.0	0.9	1.1	0.7
ΣPCB	7.6	7.1	5.6	6.6	9.7	5.9

An acceptable conformity qualitatively and quantitatively was obtained between DB-5 and DB-1701 results for most of target compounds. PCB 28 and PCB 52 made an exception because of co-eluting of matrix interferences and sub-partitioning into second silica gel fraction during the clean up. The rest of findings are presented in **tables 13** and **14** in the **appendix**.

3.2.7 Chromatograms

Sophisticated clean up procedure was developed to enhance the instrumental quantification of the target compounds. Nevertheless, most of the chromatograms were highly complex, several peaks other than those quantified were present. In the following sections chromatograms of the target compounds are discussed in details.

3.2.7.1 Chromatogram of PCB and CBz

PCBz, HCBz, and 6 PCB congeners were analyzed together in the first silica gel fraction and under the same chromatographic conditions. Their chromatograms for standard solution and sample are presented in **figures 3.4** and **3.5**, respectively. Note, some difference in y-axis's scale. Further chromatograms for CBz and PCB which were drawn using DB-1701 capillary column are presented in **figures app.1** and **app.2** in the **appendix**.

3.2.7.2 Chromatogram of organochlorine pesticides

Organochlorine pesticides chromatograms were more complex than PCB chromatograms, they separated into the second silica gel fraction which contains most of the co-extractants. Standard and sample chromatograms are presented in **figures 3.6** and **3.7**. Further chromatograms for organochlorine pesticides which were collected using DB-1701 capillary column are presented in **figures app.3** and **app.4** in the **appendix**.

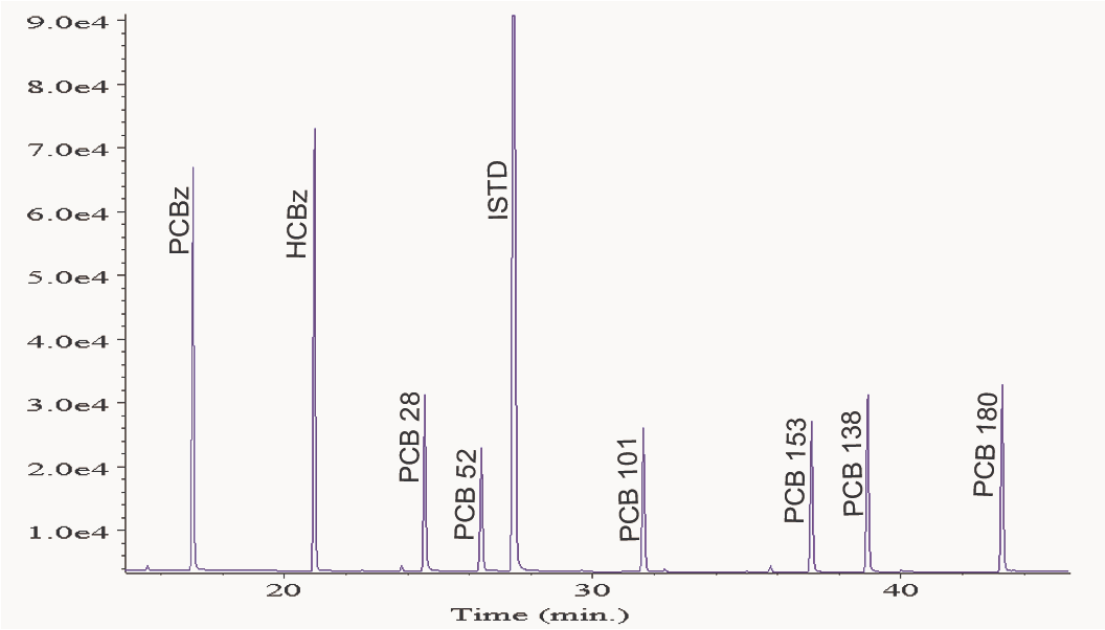


Figure 3.4. GC/ECD chromatogram using DB-5 column for standards of PCBz, HCBz and PCB.

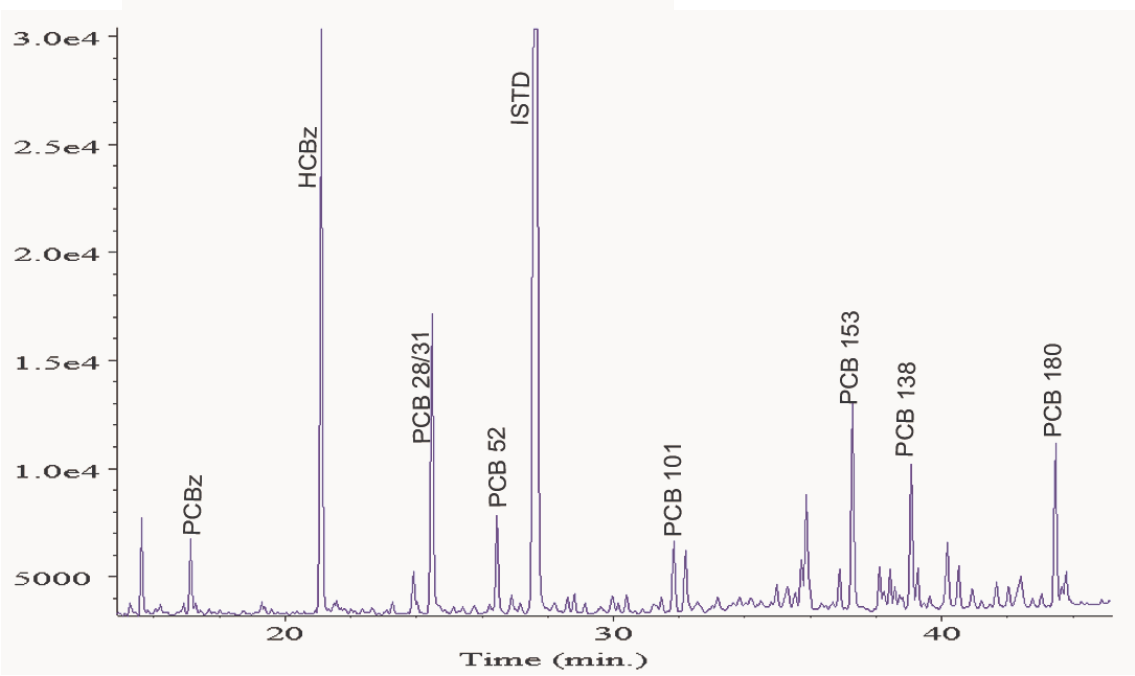


Figure 3.5. GC/ECD chromatogram using DB-5 column for sample.

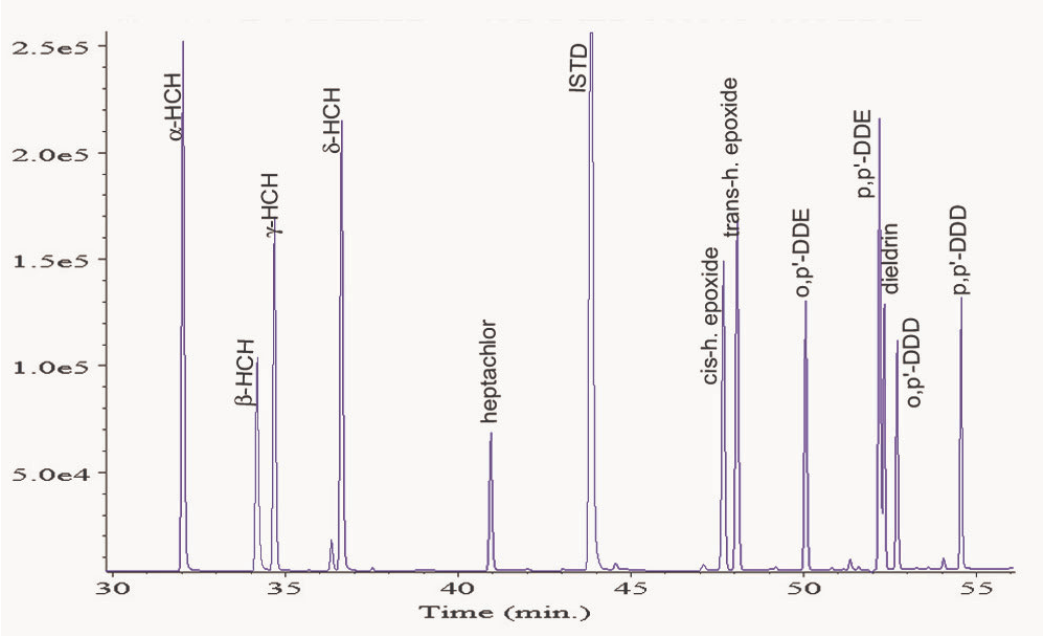


Figure 3.6. GC/ECD chromatogram using DB-5 column for standard of 12 organochlorine pesticides and their related compounds.

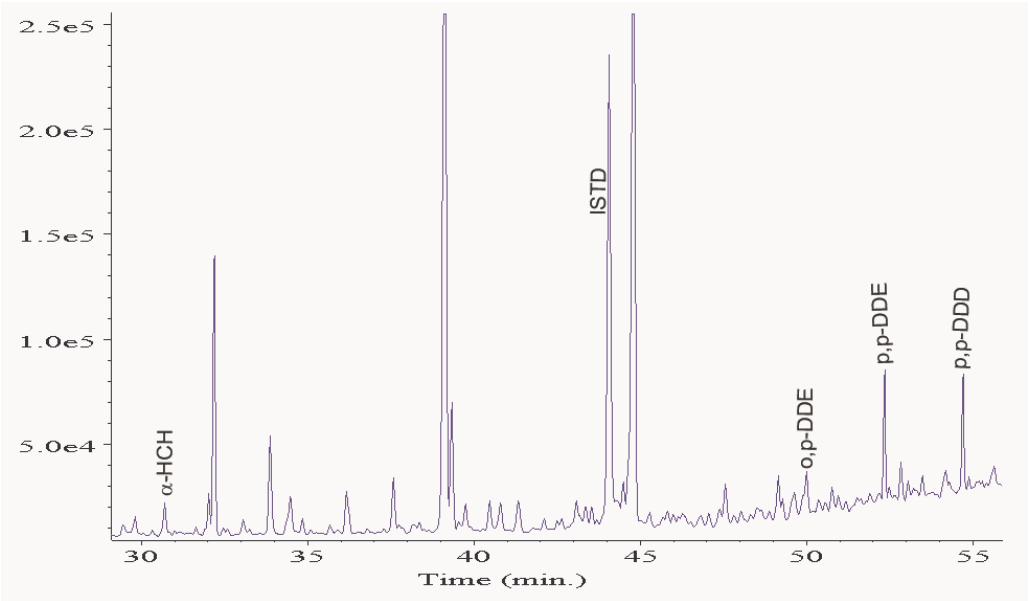


Figure 3.7. GC/ECD chromatogram using DB-5 column for a sample.

3.7.2.3 Chromatogram of PAH

The 16 PAH were determined using GC/MS operated in selected ion monitoring mode (SIM). To minimize the sample matrix effect on the GC/MS quantification the following factors were taken in consideration: firstly the calibration curves were prepared using matrix standards. Secondly, the samples diluted 10 times. Thirdly, the detected peaks were double checked using ion extract technique and the selected PAH ions peaks were manually reintegrated. Finally, the oven temperature-program (61 min) was optimized to get best base-line separation that could reduce the matrix effect, too.

The GC/MS total ion current chromatograms (TIC) for PAH standard and sample are presented respectively in **figures 3.8** and **3.9**. The TIC of the standard shows a complete base-line separation of the 16 PAH and the chromatographic elution of the 16 PAH as listed in **table 2.5** (page 41). However, the sample TIC was disturbed mostly in the retention time region between 10-20 min. This chromatographic disturbance which caused by matrix interferences in some cases could be affected the quantification of the light PAH (naphthalene-anthracene). Note different scale of y-axis's.

3.2.8 Total organic carbon

Total organic carbon was determined according to Walkley-Black´s wet oxidation method for all samples, and to confirm these results a group of selected samples were analyzed by using infrared gas analyzer method (**table 3.6**). The results showed a good conformity between the used methods. However, it was noticed that wet oxidation method obtained higher organic matter concentration than analyzer method for same sediment samples, especially for those samples which were characterized by high organic matter content. The different measuring methods yielded in different results and, therefore, the individual methods cannot replace each other indiscriminately.

The differences in organic matter content which have been obtained between the used methods can be explained as follows: Firstly, with potassium dichromate a more thorough oxidation can be obtained which includes the oxidation of different inorganic materials such as (Cl^-, NO_2^-, S_2^-, $S_2O_3^{2-}$, Fe^{2+}, and SO_3^{2-}) (Henze et al., 2002), that could enhance the measuring yield. Secondly, lower measuring yield of the analyzer method might be obtained because washing the sample with distilled water after treatment with HCl leads to some losses of the sediment organic matter into the filtrate.

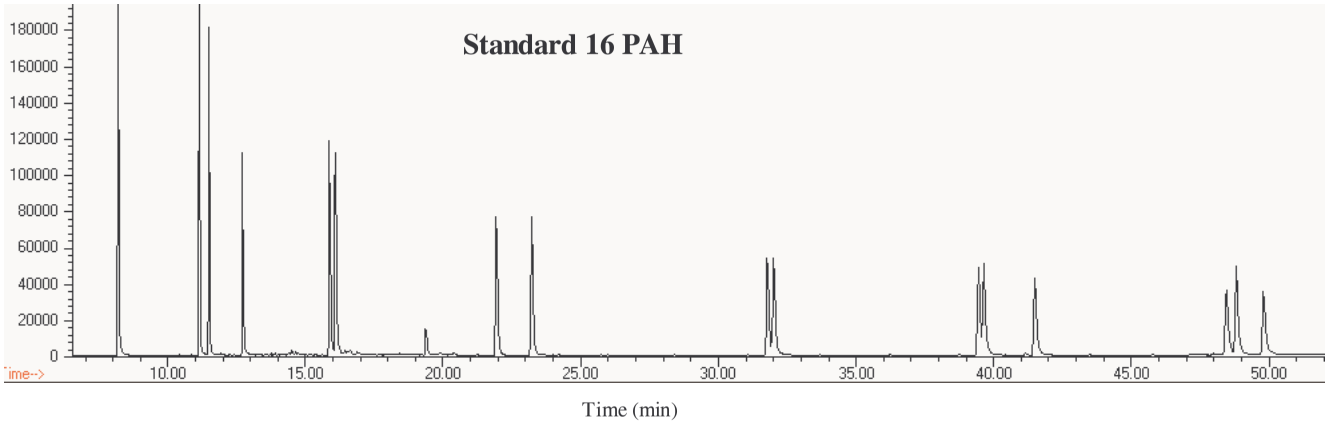


Figure 3.8. GC/MS chromatogram for 16 PAH standard.

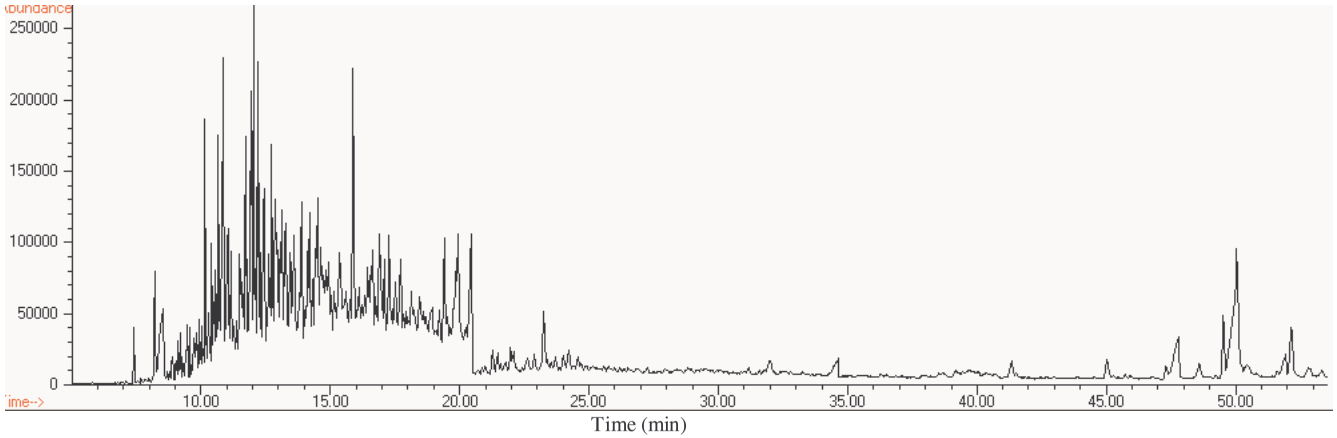


Figure 3.9. GC/MS chromatogram for sample (site D2).

Table 3.6. Quality assurance of TOC % using wet oxidation and analyzer methods.

Sample ID	TOC [%] wet oxidation	TOC [%] TOC analyzer
WR1	1.82	1.45
Z4	11.34	14.86
WBD3	5.96	4.46
FD3	17.33	12.69
Z5	10.95	11.88
AD3	23.69	10.70
BD3	25.58	16.60
WD1	2.79	2.32
WZ6	7.61	8.50
Z6	5.37	4.19

3.2.9 Samples storage and ageing

The accumulation of contaminants in sediment can be influenced by sample storage and ageing. The freezing storage of sediments to be used for future testing and analysis is not recommended because changes of organic pollutants concentration might be undergo during storage (Schuytema et al., 1989). However, it is still used by some researchers and many state and federal pollution control agencies (Rossbach et al., 1992).

Crud stable extracts were prepared fresh in Jordan for all samples to avoid storage problems, at the same time raw sediment sample materials were left frozen at –20 ^{o}C for feature uses. However, the frozen samples were taken out of the deep freezer, brought to room temperature, one part was used for further experiment and the main part was frozen again, these procedures were performed several times during the storage time (8-24 months). The analytical results have shown relative decrease in the concentration of target compounds especially for PAH content, that could be explained by biological activity and ageing problems. Whereas, other target compounds losses were not understood. Therefore, further confirmation of the results was not possible or not accurate due to the changes in the extraction behavior of the organic compounds which have been taken place. Another storage method is needed indeed for long-term storage such as storage in liquid nitrogen. Effects of storage conditions on pollutants concentrations for some selected samples are presented in **table 3.7**.

Table 3.7. Effects of storage on some pollutants concentrations, a comparison between fresh and stored sediment extracts (8-24 months between storage and reuse).

Sample	ΣPAH [µg/kg]		ΣDDTm [µg/kg]		ΣPCB [µg/kg]		Losses [%]		
	fresh	stored	fresh	stored	fresh	stored	PAH	DDTm	PCB
Z5	3153	1796	40.0	30.0	5.76	7.04	43	25	-22
AD3	1987	1199	124.0	56.0	9.61	5.76	40	55	40
WZ1	7317	3931	13.0	32.0	8.77	3.90	46	-146	56
WAD3	1061	627	28.0	18.0	6.33	2.48	41	36	61

3.3 Distribution pattern of organic matter (TOC)

The total organic carbon was determined according to Walkley-Black´s wet oxidation method and the results confirmed using TOC analyzer method. High conformity between the used methods was obtained which are discussed in detail in section 3.2.8. The TOC amounts were ranged over 1.43-28.09 % ± 8.13 % with an average 10.33 % for summer, and 0.70-34.70 % ± 7.48 % with an average 6.08 % for winter. The variability of organic matter content is dependent on type of anthropogenic activity at site and amount of waste effluent as well as on the rainfall quantities. Sediments total organic carbon and other sample physical properties for both sampling periods are presented in **table 2.6** (page 45).

The individual distribution pattern of TOC for whole samples in both seasons is presented in **figure 3.10**. Wadi Dhuleil contained 2-6 times higher organic matter than the other categories. That might be explained as a consequence of the direct discharge of the As-Samra WSPs effluents. The maximum TOC values were found as 28.1 % and 34.7 % at sites D2 and WD3 for summer and winter seasons, respectively. It was noticed that samples for summer season have contained organic matter by about 3 times higher than for winter season. That might be explained by the rainfall quantities, the summer sampling periods came after few mm of rainfall which might be caused the first wash out event. However, the winter sampling periods came after exceeding the annual average winter rainfall. Therefore, wash out of pollutants from residential and industrial areas has been taken place during the first rainfall event, then the pollutants washed out from the sediments during wet season.

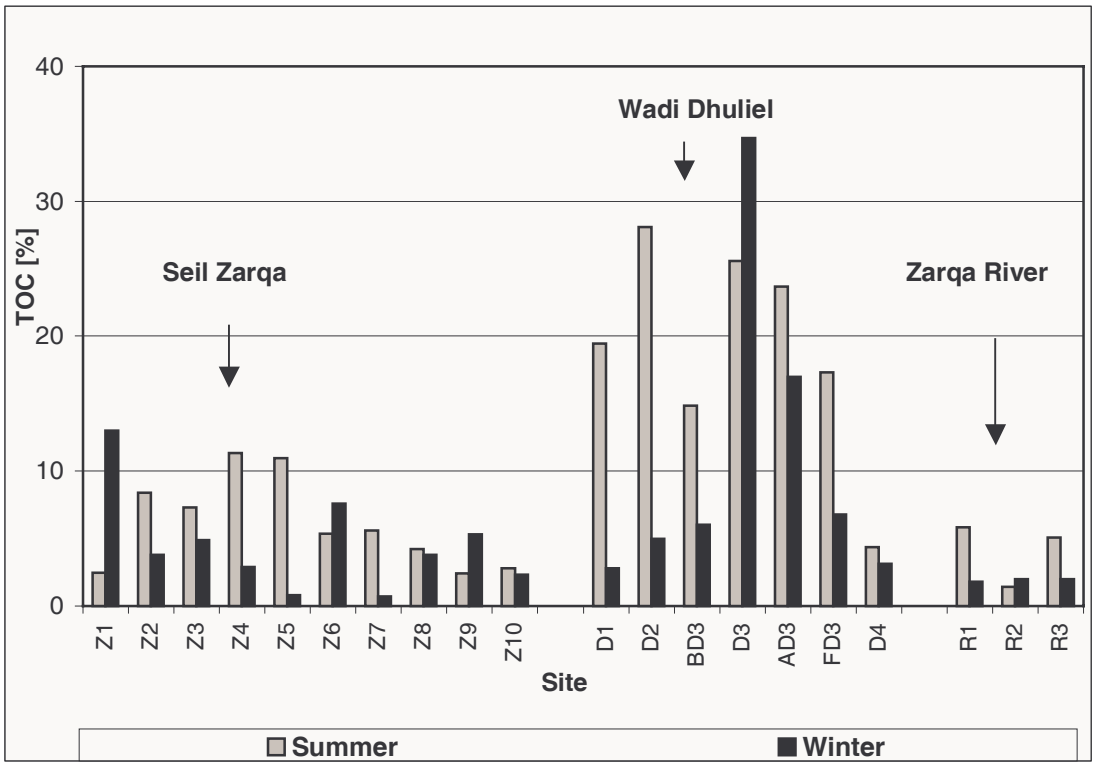


Figure 3.10. Individual distribution pattern of total organic carbon (TOC) in sediment for summer and winter seasons.

The incident ratios for the total organic carbon were calculated: 70 % of the sediment samples in summer season contained total organic carbon more than 5 %, 25 % between 2 % and 5 %, and only 5 % reported TOC less than 2 %. However, for winter season, 33 % of the samples reported TOC more than 5 %, 43 % between 2 % and 5 %, and 24 % reported TOC less than 2 %. In addition, it was noticed that the total organic carbon of the sediments decreased with the direction of water flow and far away from the point source pollution sites such as the leakage points from the wastewater-transport pipeline to As-Samra and As-Samra WSPs. For instance, sites R1, R2 and R3 which were located from 12 to 27 km away from As-Samra WSPs have shown lower organic matter content compared to other sites which are located nearby the point source pollution.

The mean organic matter content in sediments ranged from 4.10 to 19.05 % for summer and from 1.84 to 10.76 % for winter. It is noticed that higher concentrations of TOC in summer are reported than in winter for the three sampling categories. Their mean organic matter is presented in **figure 3.11**. Generally, significant correlations were observed between TOC and the concentrations of the hydrophobic pollutants in sediments. The present work findings were found to be in agreement with results

obtained by Kukkonen (1996, 1997), Xu et al. (2000), Jeong (2001) and other studies which contributed to the important role of organic carbon in the accumulation and flocculation of hydrophobic compounds in sediments.

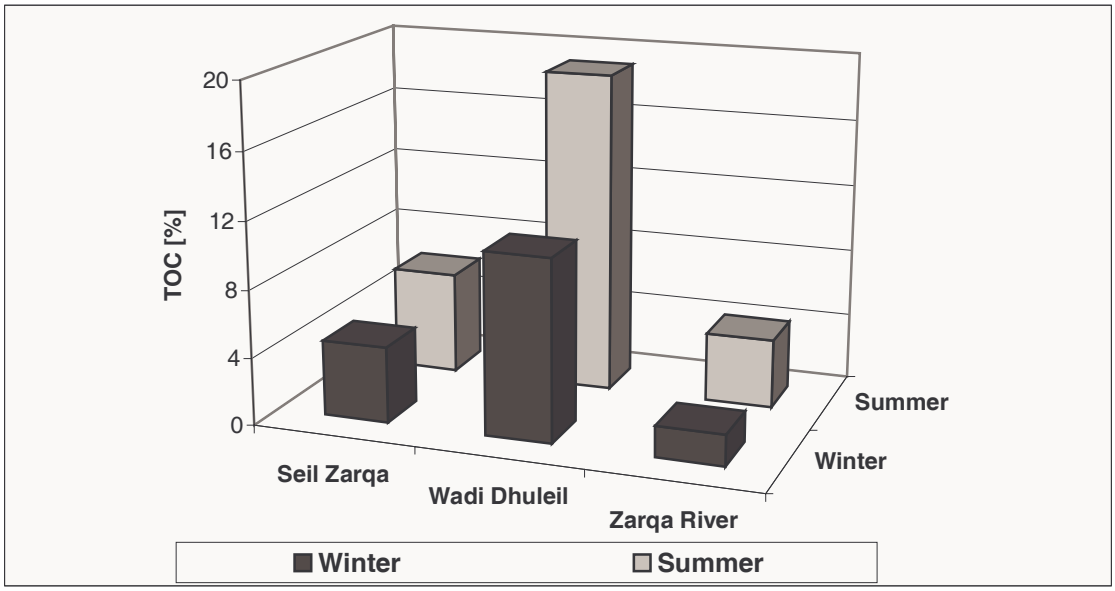


Figure 3.11. Mean concentrations of organic matter for three sampling categories during both sampling periods.

3.4 Particle size analysis

Sediment particle size distribution and organic matter have been found to play a major role in the partitioning of hydrophobic organic xenobiotics between water and solid phases (Kukkonen and Landrum, 1996; Paolis and Kukkonen, 1997). The sediment particle size analysis was obtained by hydrometer method for both sampling periods and the results are presented in **tables 3.8** and **3.9**, respectively. The sediment texture among all collected samples ranged from sandy clay loam to loamy sand. The clay percentage varied widely for summer season which ranged from 8.1 to 62.6 % ± 14.3 %, however, less variation was obtained in winter season which ranged from 10.6 to 50.8 % ± 8.1 %. That might be pointed to homogenous texture of sediments in wet season better than in dry season, where new sediments are brought to the river drainage system which are originated from erosion and wash out processes. The same phenomena were observed for sand fraction which ranged to 24.4-83.5 % ± 15.1 % and 48.5-86.7 % ± 9.7 % for dry and wet seasons, respectively. The silt fraction was the smallest portion of the sediments texture for most of samples. It ranged to 5.5-27.3 % ± 7.3 % for summer and 0.0-22.2 % ± 6.4 % for winter.

Table 3.8. Sediment fraction analysis, sampling period 22-26/11/2001 (summer season).

Site	Sediment fraction analysis			
	Clay [%]	Silt [%]	Sand [%]	Texture
Z1	22.47	7.15	70.38	sandy clay loam
Z2	23.68	20.45	55.87	sandy clay loam
Z3	32.54	19.40	48.06	sandy clay loam
Z4	-	-	-	n.a*
Z5	25.76	26.35	47.89	sandy clay loam
Z6	17.91	22.25	59.84	sandy loam
Z7	48.23	27.33	24.44	sandy clay loam
Z8	15.14	22.97	61.88	sandy loam
Z9	13.58	26.64	59.78	sandy loam
Z10	19.47	24.08	56.45	sandy clay loam
D1	62.56	5.47	31.67	sandy clay loam
D2	22.55	16.91	60.54	sandy clay loam
BD3	-	-	-	n.a
D3	8.08	11.19	80.73	loamy sand
AD3	43.72	9.14	47.14	sandy clay
FD3	19.88	8.89	71.22	sandy loam
D4	-	-	-	n.a
R1	11.21	15.48	73.31	sandy loam
R2	8.52	8.02	83.46	loamy sand
R3	23.49	17.24	59.27	sandy clay loam

* n.a: not analyzed

Table 3.9. Sediment fraction analysis, sampling period 26-29/01/2002 (winter season).

Site	Sediment fraction analysis			
	Clay [%]	Silt [%]	Sand [%]	Texture
WZ1	20.42	6.88	72.70	sandy clay loam
WZ2	22.27	14.55	63.18	sandy clay loam
WZ3	23.91	15.50	60.59	sandy clay loam
WZ4	21.35	14.15	64.50	sandy clay loam
WZ5	16.85	3.52	79.62	sandy loam
WZ6	22.49	16.21	61.30	sandy clay loam
WZ7	10.56	2.77	86.67	loamy sand
WZ8	17.12	8.82	75.06	sandy loam
WZ9	25.88	19.54	54.58	sandy clay loam
WZ10	14.82	6.65	78.53	sandy loam
WD1	19.01	0.51	80.48	sandy loam
WD2	26.56	12.47	60.97	sandy clay loam
WBD3	16.88	13.97	69.15	sandy loam
WD3	50.84	0.67	48.49	sandy clay
WAD3	30.86	0.0	69.14	sandy clay loam
WFD3	18.67	17.10	64.23	sandy loam
WD4	16.99	5.56	77.45	sandy loam
WR1	16.80	6.87	76.33	sandy loam
WR2	19.09	22.15	58.76	sandy loam
WR3	16.82	8.56	74.62	sandy loam
WR4	12.76	6.86	80.38	loamy sand
Ref.site	20.89	9.58	69.63	sandy clay loam
l.waste	-	-	-	-

3.5 Sediment's pH

The sediment pH value does not greatly affect the binding capacity of the humic substances for most of hydrophobic pollutants. The organic carbon partition coefficient (K_{oc}) represents the partitioning of organic contaminants between water and organic carbon phases. It was proved that K_{oc} values for benzo[a]pyrene were weakly affected with pH range over 5.0 and 8.0 (Paolis and Kukkonen, 1997). The pH values measured for both sampling periods are presented in **table 2.6**. They ranged from 6.23 to 8.21 ± 0.40, where slightly differences were observed among the pH values for all samples. More than 80 % of the samples shown pH values between 7.0 and 8.0. That might reflect the parent material's composition for dust, soil, and sediments which are characterized by high carbonate ($CaCO_3$) content ranged from 20 to 25 % (Kadry, 1972; Jiries et al., 2002). The pH values are demonstrated in **figure 3.12** for summer and winter sampling periods.

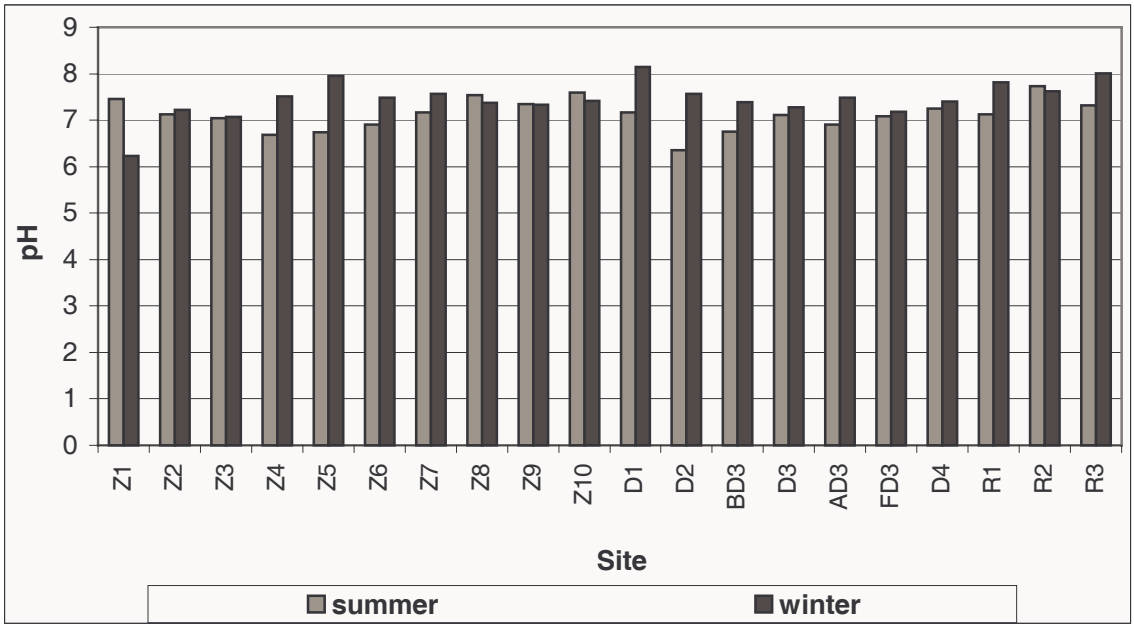


Figure 3.12. pH values presented for both sampling periods.

3.6 Distribution pattern of PAH

The concentrations of PAH are presented for sediments for summer and winter sampling periods as raw data in **tables 1 and 2** in **appendix**, respectively. The presence of "non-contaminated" reference site provides the chance to evaluate the magnitude of the environmental contamination in the studied sediments. However, all

sampling sites have illustrated total concentration of PAH higher than the reference sediments site (28 µg/kg) which was located far away from heavy from investigated area.

The distribution pattern of the total concentration of PAH (sum of 16 priority pollutants) is presented in **figure 3.13**. They ranged from 69 to 7319 ± 1331 µg/kg on dry weight basis among all samples. The maximum concentration was found at site Z5 (3414 µg/kg d.w.) for summer season. However, site WZ1 showed extremely high concentration of ΣPAH (7319 µg/kg d.w.) in winter season, therefore, its value was excluded from the average calculation. The minimum concentration was determined down stream of Zarqa River at site R2 (69 µg/kg d.w.). The 16 PAH were detected in 94.4 % of the analyzed samples for summer season and in 89.4 % for the winter samples. The distribution pattern of total PAH concentrations have appeared in summer season at 2-3 times higher concentration levels than for winter season. This might be explained as dilution effect that has been taken place during wet season. While, the summer sampling was carried out after first wash out event which might be brought to the drainage system heavy polluted sediments load. Then, after washing out the sediments in wet season, the concentrations of PAH were detected in lower levels. The distribution pattern of PAH are separately discussed for each sampling category and period.

3.6.1 Summer season

The sampling period which was carried out on November 2001 represents the end of summer season, it might be short-time after wash out events in the studied area, where the rainfall intensity is responsible for the wash load. Firstly, for category Z, the total concentrations of PAH were dramatically increased at the first sampling sites along Seil Zarqa until they reached maximum concentration at site Z5 (3414 µg/kg). These sites were affected by heavy industrial activities as well as high traffic roads at Arrusseifa area. Then, PAH concentrations continually decreased until they reached minimum concentration down stream of this tributary at site Z10 (93 µg/kg). Therefore, limited transport of the PAH along the drainage system was observed that might be explained due to the limited water flow during dry season. The total concentration of PAH were significantly correlated to the total organic matter (R^2=0.95).

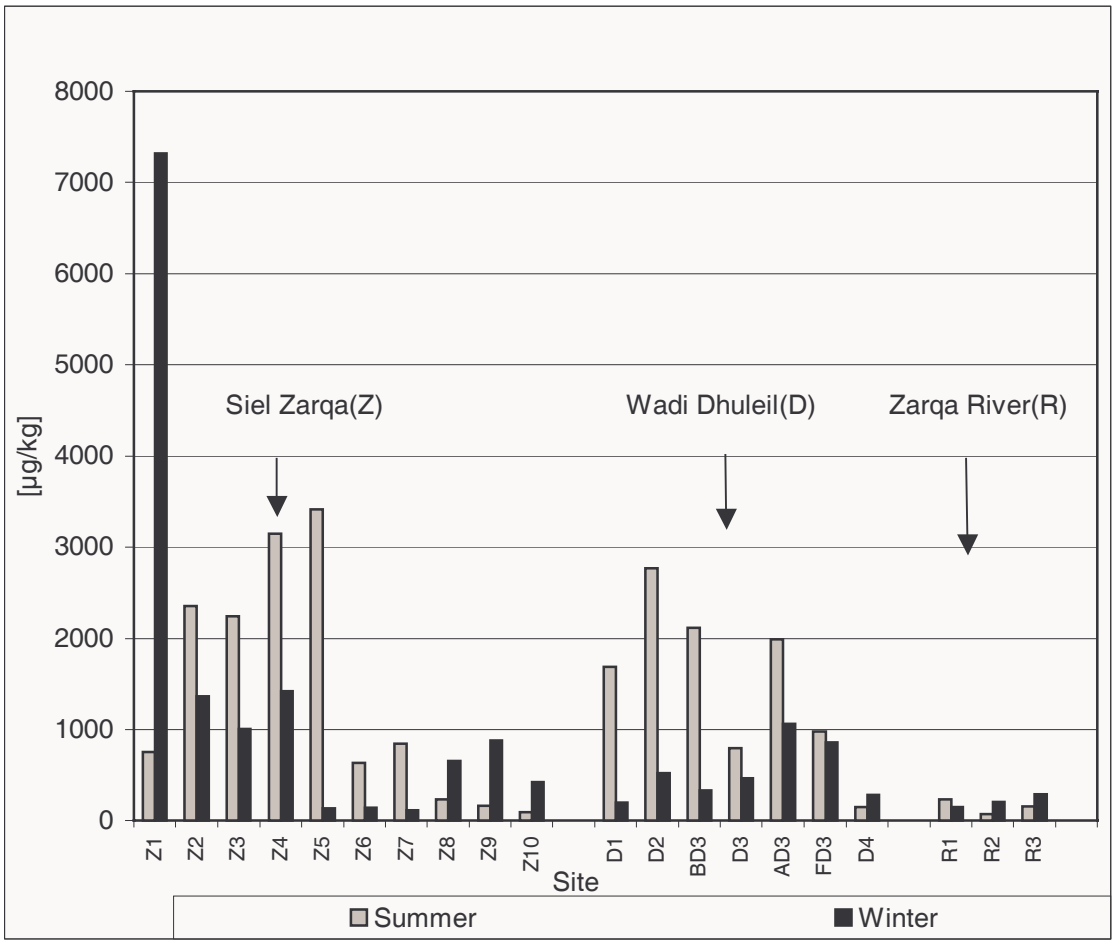


Figure 3.13. Distribution pattern of ΣPAH for summer and winter seasons, Seil Zarqa Z1-Z10, Wadi Dhuleil D1-D4, and Zarqa River R1-R3, (ΣPAH: summation of 16 PAH in µg/kg dry weight).

Secondly, category D has shown particularly high total concentrations of PAH, because of the wastewater effluents and less dilution potentials during dry season. The maximum ΣPAH concentration was reported at site D2 (2772 µg/kg), which is located at high traffic road (Zarqa-Mafreq road), then they decreased until site AD3 (1987 µg/kg) which was located 20 m after effluent of the paper mill. The analysis of this paper mill wastewater has demonstrated high total organic carbon (97.5 %) and ΣPAH (1935 µg/kg). After about 800-900 m from site AD3, the concentrations of PAH steadily decreased at sites FD3 and continued to decrease until reached minimum concentration at site D4 (150 µg/kg). As a consequence of high TOC variability within the studied samples, a relatively weak correlation (R^2=0.63) was obtained between TOC and ΣPAH.

Finally, category R has found relatively low ΣPAH concentration levels and they remained at the same level along the sampling sites. The total PAH concentrations ranged from 69 to 234 µg/kg dry weight. A limited transportation of PAH as well as more degradation processes have been taken place down stream of Zarqa River, that can be concluded. In addition, significant correlation was observed between TOC and ΣPAH (R^2=0.95).

3.6.2 Winter season

The sampling period which was carried out on January 2002 represents the winter season. Total 16 PAH concentrations on a dry weight basis ranged over 111 to 1419 µg/kg. However, the extreme concentration was found at site WZ1 (7319 µg/kg), where it is located 6 km northeast of Zarqa River source. It is the first site along Seil Zarqa which receives wash out waters from whole Amman catchment area. The sediments at this site were characterized by high organic matter content (13 %), sandy clay loam texture and of dark black color. Therefore, wash out waters settled most of their biomass at this site. The lowest concentration was determined at site WZ7 (111 µg/kg) which contained the lowest organic matter. For Seil Zarqa, the total concentration of PAH in sediment progressively decreased with the direction of the water flow along sampling sites. For example, the ΣPAH content up stream at site WZ1 was 17 times higher than site WZ10 down stream. Organic matter was significantly correlated to ΣPAH (R^2=0.82).

Due to the wastewater effluents as well as high TOC content category WD contained relatively higher total concentrations of PAH than other categories WZ and WR, they varied from 282 to 1062 µg/kg. However, it was clear that lower concentrations of PAH in winter than in summer were found, that might be caused by the wash out of pollutants during wet season. The concentration levels of ΣPAH remained at the same level at sites WD1, WD2, WBD3 and WD3, until they reached maximum concentration at site WAD3 (1062 µg/kg). Then, concentration levels of ΣPAH decreased again down stream of Wadi Dhuleil at sites WFD3 (859 µg/kg) and WD4 (282 µg/kg). These meets that results for summer season, therefore, a point source pollution (at the paper mill effluents point) was detected at site WAD3. No correlation was obtained between TOC and ΣPAH for this category. Finally, after confluence point of WZ and WD categories, WR category shown similar trend of ΣPAH concentrations along the sampling sites.

They ranged from 111 to 288 µg/kg. In addition, the total concentrations of PAH were significantly correlated to the organic matter content (R^2=0.84).

3.6.3 Individual distribution of PAH

The mean concentration of individual PAH compounds for Seil Zarqa tributary, Wadi Dhuleil, and Zarqa River compared in both sampling periods are presented in **figures 3.14**, **3.15** and **3.16**, respectively. The average concentration of PAH compounds for Seil Zarqa ranged from 14 µg/kg d.w. for dibenzo[a,h]anthracene to 370 µg/kg d.w. for phenanthrene in summer and from 3 for dibenzo[a,h]anthracene to 196 µg/kg d.w. for phenanthrene in winter. For the second tributary, the average concentration ranged from 13 for benzo[k]fluoranthene to 497 µg/kg d.w. for phenanthrene in summer and in winter from 2 for indeno[1,2,3,4,cd]pyrene to 184 µg/kg d.w. for phenanthrene. Finally, for Zarqa River the average concentrations ranged from 4 for indeno[1,2,3,4,cd]pyrene to 28 µg/kg d.w. for pyrene in summer, and from 3 for benzo[k]fluoranthene to 50 µg/kg d.w. phenanthrene in winter season.

The individual distribution of PAH for summer season were in descending order: phenanthrene > pyrene > fluorene > naphthalene > fluoranthene > chrysene > anthracene > acenaphtene > benzo[g,h,j]perylene. However, similar trends of individual PAH compounds were observed also for winter season. The dominated PAH in descending order were: phenanthrene > pyrene > fluorene > fluoranthene > chrysene > naphthalene > benzo[b]fluoranthene > acenaphtene > anthracene > benzo[g,h,j]perylene. The rest of PAH were detected in traces.

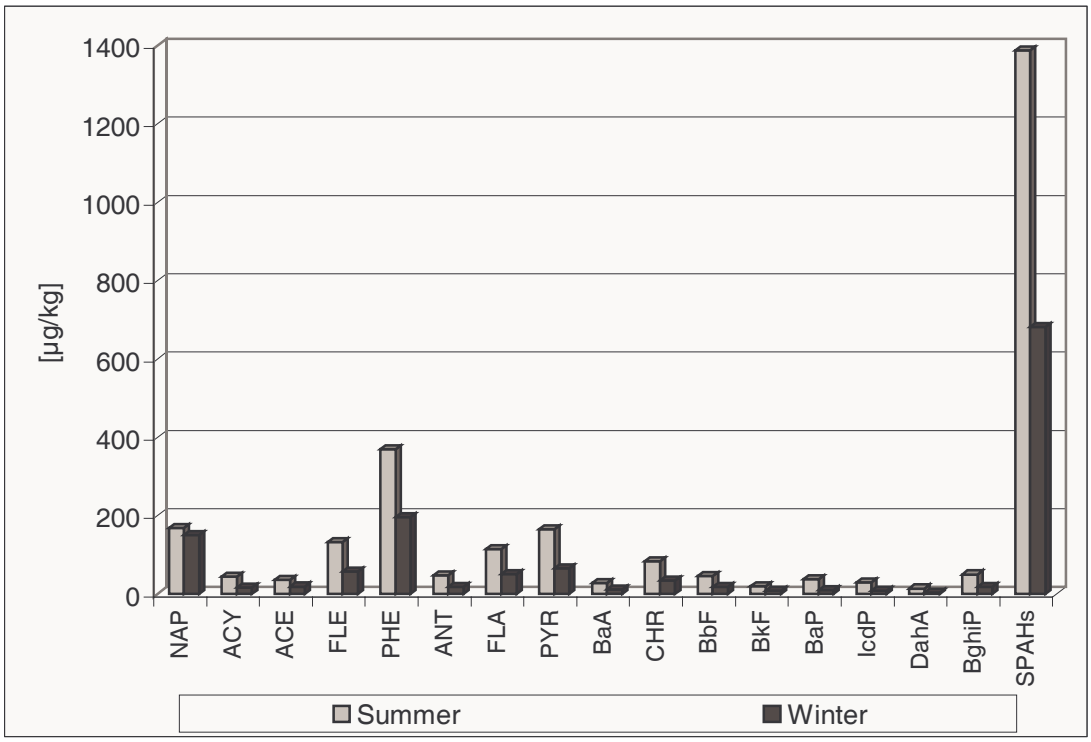


Figure 3.14. Individual distribution of PAH compounds for Seil Zarqa (Z2-Z10) and sum of 16 PAH (SPAH).

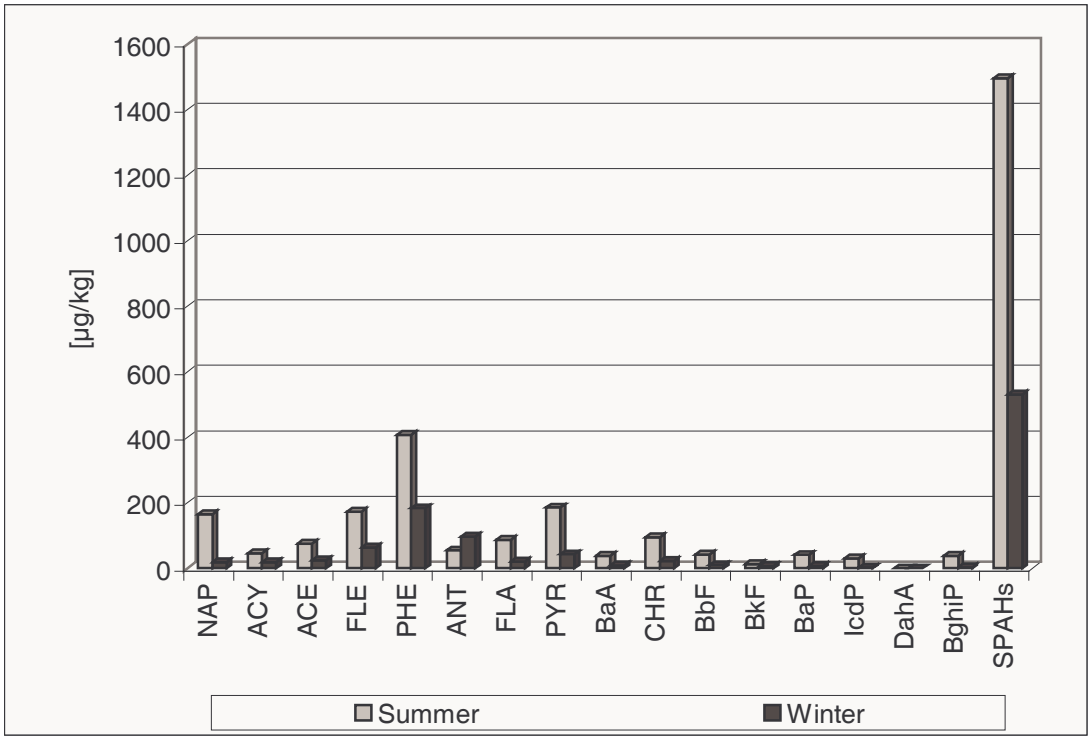


Figure 3.15. Individual distribution of PAH compounds for Wadi Dhuliel (D1-D4) and sum of 16 PAH (SPAH).

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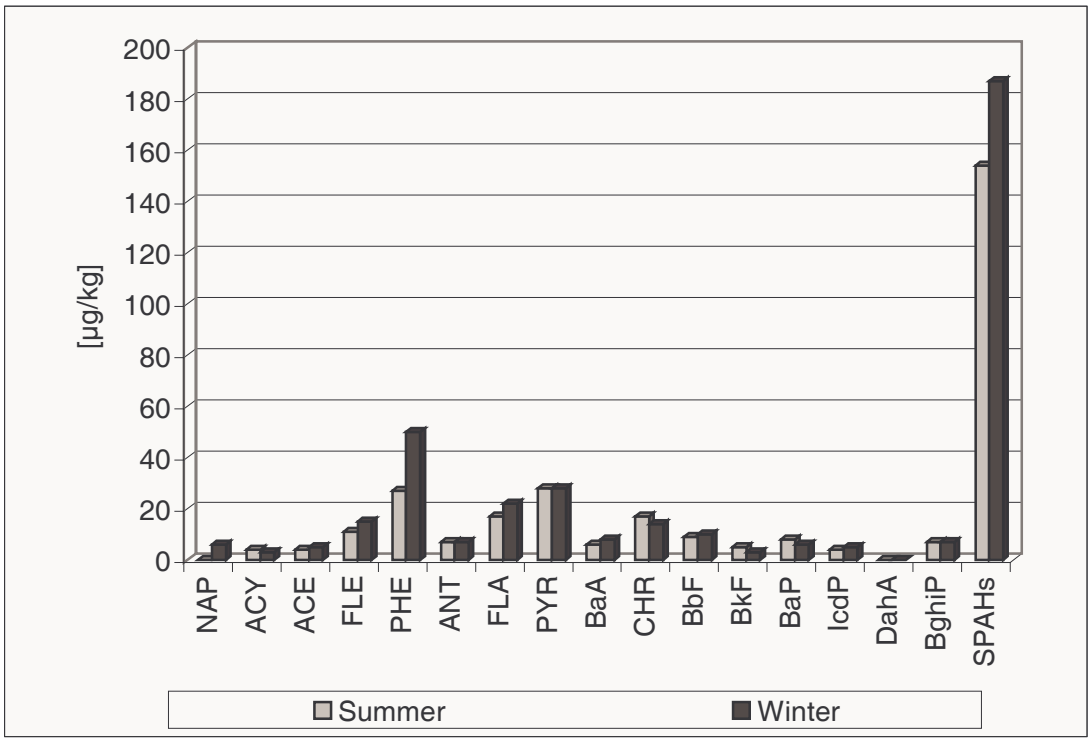

Figure 3.16. Individual distribution of PAH compounds for Zarqa River (R1-R4) and sum of 16 PAH (SPAH).

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3.6.4 Profiles of PAH

The physical and chemical properties of PAH are responsible for their mobility in the environment. The road runoff pollution by PAH was contributed to river sediments (Krein and Schorer, 2000). They found that 2-3 rings PAH molecules accumulate more rapidly than 4-6 rings PAH molecules, and the smaller ring systems are enriched mainly in fine sand fraction. The overall patterns of the road runoff material from metals and PAH at the Olewiger Bach catchment in Germany and the Olewiger Bach bottom sediments appear similar. For example, **table 3.10** presents the average concentrations of selected PAH in different grain-size fractions of eight road runoff material samples and eight river sediment samples. In addition, impacts of urban runoff on particulate metal concentrations during seasonal variation was studied in Seine River in France, the results have shown similar trends of metals for the runoff and the river waters (Estèbe et al., 1998). These finding were supported by Kukkonen and Landrum (1996) and Fu et al. (2001). Therefore, fresh sediment profiles could be pointed to the source of PAH, especially the street traffic and urban wash out loads.

Table 3.10. Average concentrations of selected PAH in different grain-size fractions of eight road runoff material samples and eight river sediment samples (Krein and Schorer, 2000).

	Grain size [µm]					
	< 2	**2-6.3**	**6.3-12.5**	**12.5-20**	**20-63**	**63-200**
Street runoff						
Fluoranthene [µg/kg]	350	1622	1554	1155	1078	1958
Benzo[ghi]pyrene [µg/kg]	139	710	541	217	287	281
Organic carbon [%]	14	22	25	27	19	30
River sediments						
Fluoranthene [µg/kg]	232	380	516	620	288	813
Benzo[ghi]pyrene [µg/kg]	121	152	138	161	97	206
Organic carbon [%]	2.9	4.3	3.6	2.5	0.9	5.7

In Jordan, the 16 PAH have been studied for road dust (Jiries, 2003) as well as in rain and runoff in Amman area (Jiries et al., 2003). The urban roads dust samples were collected in August 2001 and the runoff and rain samples collected from November 1999 to April 2000. The total concentration of the PAH in dust ranged from 13240-49960 µg/kg and the distribution pattern is dominated by 4-6 ring systems. These findings reflect the dry climatic conditions for summer in Jordan. In addition, they found that PAH content is significantly correlated to the total organic matter. However, the total concentration of PAH ranged from 46 to 975 ng/L and from 66 to 1421 ng/L for rain and runoff waters, respectively. The highest concentrations of PAH were observed in the first rain events which was in November 1999. Totally, the overall distribution pattern of 16 PAH for both rain and street runoff characterized by 2-3 rings molecules (55 % is 2-3 rings system and 45 % is 4-6 rings system).

Classification of the PAH findings into two structure classes 2-3 rings and 4-6 rings systems have shown the following facts concerning the sedimentation profiles: Firstly, down stream of Zarqa River was dominated in both seasons by older sediment profiles (4-6 rings system). That might be explained as photo-degradation and volatilization processes for the small PAH rings system which have been taken place down stream considering that limited transport of PAH during summer season. Secondly, in the winter season fresh sediment profiles (2-3 rings system) appeared which might be caused by the wash out load of roads and residential areas especially that Zarqa River is used to transport surface runoff of Amman area to King Talal Reservoir. Finally, the sediment texture from Zarqa River was dominated by sandy clay loam to sandy loam textures in both seasons. This might be the reason for the enrichment of PAH in fine sandy and silty fractions, while, clay fraction is always poor with PAH (Krein and

Schorer, 2000). The profiles of PAH along the investigated area for summer and winter seasons, respectively are shown in **figures 3.17.a** and **3.17.b**. The distribution pattern of 16 PAH in the present work were found in a good agreement with Jiries et al. (2003) findings.

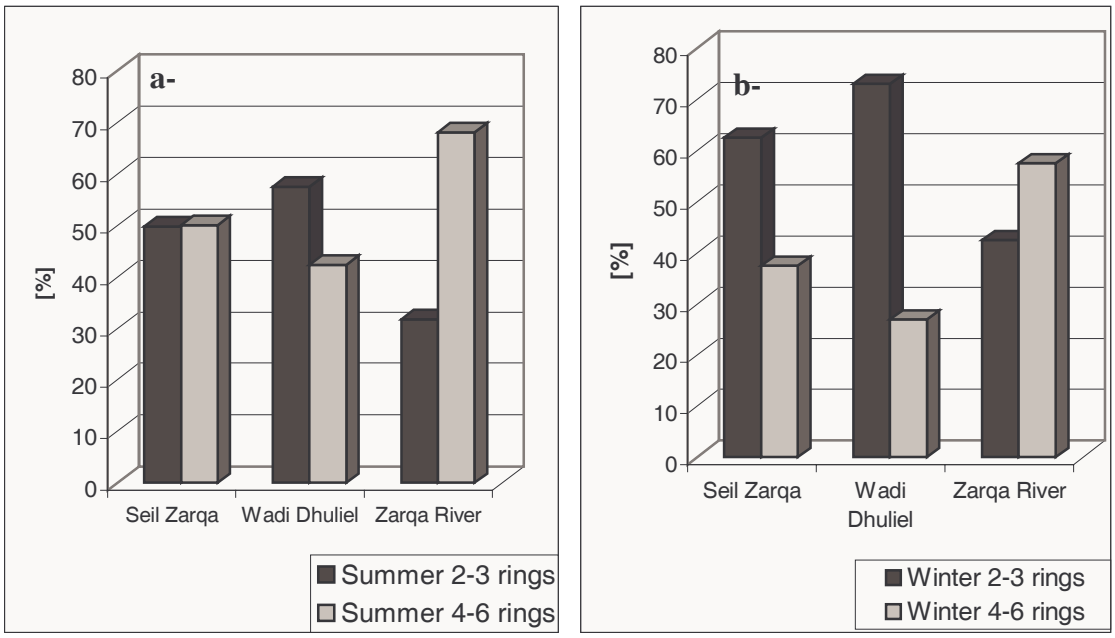

Figure 3.17. **a-** PAH profiles for summer, **b-** PAH profiles for winter.

3.6.5 PAH findings from different countries

Findings of the PAH concentrations in sediment for the present work were compared to other findings of PAH concentrations in sediments from different countries. They are summarized in **table 3.11**.

Table 3.11. Average concentration or range of US EPA 16 PAH detected in sediments from different countries in µg/kg dry weight.

Site	ΣPAH	Reference
Braunschweig port/Germany	8960	Kolb, 1994
Florida/USA	25000	Miles and Delfino, 1999
Pearl River/China	408-10811	Fu et al., 2001
St. Lawrence River/Canada	440-1050	Coakley et al., 1993
Yangtse River/China	16-765	Xu et al., 2000
Santander Bay/Spain	20-344600	Viguri et al., 2002
Karak/Jordan	3-23	Jiries et al., 1999
Present work (December, 2000)	58-3664	-
Present work (November, 2001)	69-3414	-
Present work (January, 2002)	111-1419	-

The concentration of PAH for the present work were found at lower levels than those obtained in Branschweig port at Oker River in Germany, Pearl River in China and St. Lawrence River in Canada. Furthermore, they were found at Florida in USA and Santander in Spain by factor 28 much higher than those obtained in the present work. However, they were determined at higher levels than in sediments from Yangtse River in China and stream sediments at Karak in Jordan. One can conclude that higher levels of PAH were recorded often in much more urbanized and industrialized countries.

Organic pollutants are not yet regulated worldwide in sediments. Whereas, the sediment quality can be assessed by measuring the pollutant's concentration in sediment, performing toxicity tests and determine the bioaccumulation potentials. Nevertheless, standards for other environmental compartments such as for sewage sludge and soils can be compared in this context. For example, the total 16 PAH concentration is regulated for sewage sludge for agricultural use in European Union as 6.0 mg/kg on dry weight basis (EU, 2000) and in Switzerland for soil the total concentration of PAH should not exceed 0.5 mg/kg of dry soil (DSBR, 1998).

3.7 Polychlorinated biphenyls (PCB)

The recovery rates of 6 PCB congeners ranged from 81 to 109 % and their minimum detection limit which was based on signal to noise ratio (3:1) varied from 0.12 to 0.15 µg/kg. Precision of the analytical results was acceptable (RSD < 20 %) for PCB 101, PCB 138, PCB 153 and PCB 180. However, PCB 28 and PCB 52 made an exception due to the co-eluting and partitioning problems. The present analytical procedure separated PCB from PAH and organochlorine pesticides by efficiency exceeded 96 %. However, flow rate and sample matrix could be caused a partition problem for PCB 28 and PCB 52 during silica gel clean up into the second fraction. The partitioning ratio of PCB 28 and PCB 52 between the first and second silica gel fractions might be in worst cases 80:20 %. The same analytical procedure was applied by Jang and Li (2001). They have separated successfully PCB and PAH in sediment samples using fully activated silica gel column in order to enhance the quality of the instrumental analysis.

The concentrations of the PCB in sediments are given in **tables 3** and **4** in the **appendix** for both sampling periods. More than 97 % of the 6 PCB congeners analyzed have been detected in all samples analyzed. The analytical results showed low variability in the total concentration of the PCB for both sampling periods. The total concentrations of the PCB congeners (ΣPCB) ranged from 1.72 to 9.69 ± 2.04 µg/kg

dry weight in the summer and from 1.73 to 8.77 ± 1.99 µg/kg dry weight in the winter. The maximum concentrations of ΣPCB were found at sites BD3 (9.69 µg/kg dry weight) and WZ1 (8.77 µg/kg dry weight) for summer and winter seasons, respectively. However, the minimum total concentrations were determined down stream of Zarqa River at sites R2 (1.72 µg/kg d.w.) and WR4 (1.71 µg/kg d.w.).

The distribution pattern of the total concentration of PCB congeners for both sampling periods are presented in **figure 3.18**. The concentration levels for total PCB appeared close to each other during both sampling periods and the analytical results showed low concentration variability. That might be explained as a consequence of permanent industrial waste disposal or discharges which serve as main source of PCB pollution in aquatic environment. The industrial waste could be introduced to the studied aquatic environment, either via As-Samra wastewater stabilization ponds or by direct discharge into the river drainage system. In addition, the seasonal variation did not influence the PCB concentrations and distribution pattern.

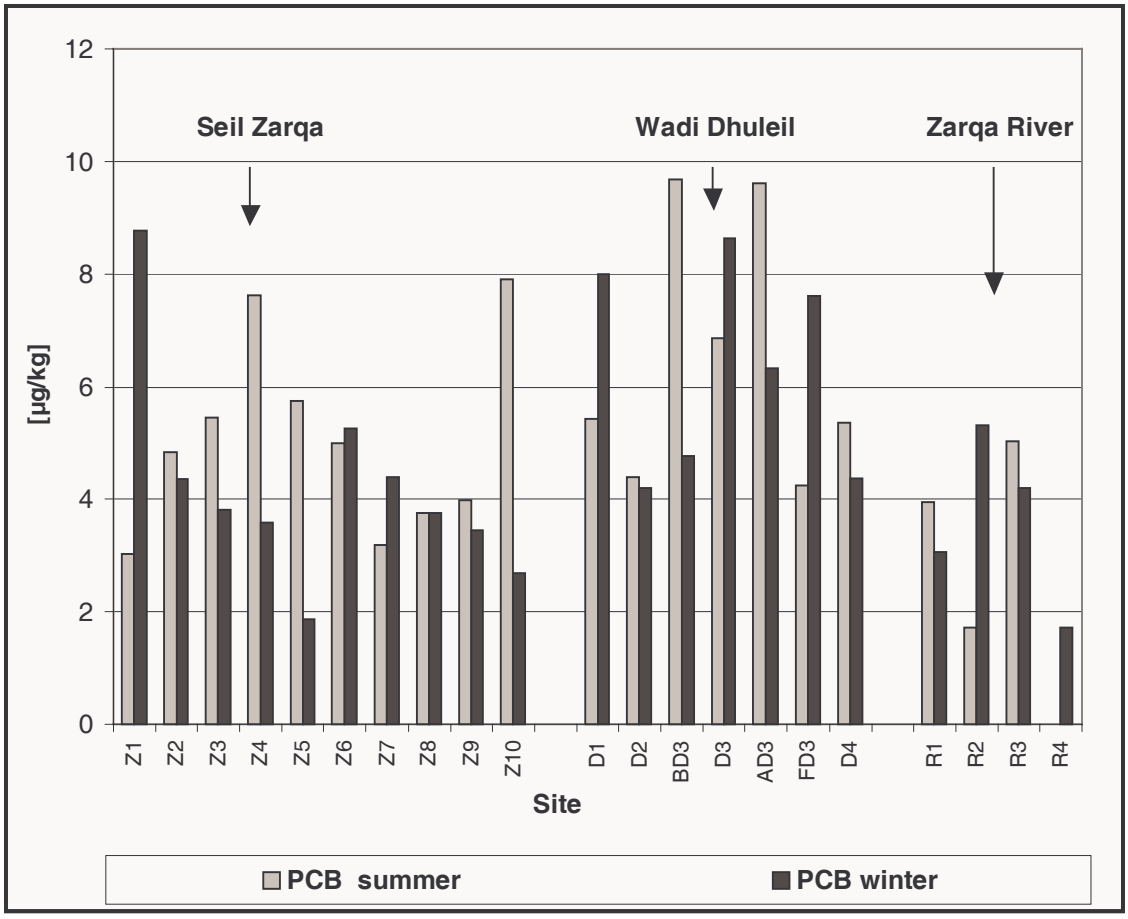

Figure 3.18. Distribution pattern of ΣPCB for summer and winter seasons, Seil Zarqa Z1-Z10, Wadi Dhuleil D1-D4, and Zarqa River R1-R3, (ΣPCB : summation of 6 PCB congeners in µg/kg d.w.).

The total PCB concentration appear in **figure 3.18** similar for Seil Zarqa and Wadi Dhuliel tributaries, whereas, relatively lower concentration levels were found down stream of Zarqa River. The distribution pattern of PCB were dependent on the organic matter content. Whereas, the total polychlorinated biphenyls were correlated significantly to the total organic carbon for winter, they weakly correlated in summer. The correlation coefficients between PCB and TOC were: 0.88, 0.56 and 0.95 for winter and 0.44, 0.04 and 0.88 for summer seasons for Z, D and R categories, respectively.

3.7.1 Individual PCB distribution

The individual distribution pattern of PCB congeners are presented as average concentrations in **figures 3.19, 3.20** and **3.21** for Seil Zarqa, Wadi Dhuleil, and Zarqa River for both sampling periods, respectively. Generally, Wadi Dhuleil indicated average concentrations of the 6 PCB higher than other categories, that might be due to high organic matter. PCB 28 was the predominated congener in all samples, mostly, it was co-eluted with PCB 31 which leads to an interfering high detected signal.

The individual PCB distribution pattern were found relatively similar for both seasons. They mainly depended on the organic matter content. However, the distribution pattern for summer season were in descending order: PCB 28 > PCB 138 > PCB 153 > PCB 180 > PCB 101 > PCB 52, while for winter season: PCB 28 > PCB 138 > PCB 153 > PCB 52 > PCB 180 > PCB 101. In addition, t-Test (Student's test) was performed which is typically used to compare the means of two populations and to decide if there is a significant difference between the tested means with for example 95 % confidence interval (α = 5 %), where α represents the percentage error. The statistical results have shown there is not a significant difference in the sample means. The differences could not be detected due to large variability and small sample size. Therefore, the *t-Test* was not applied for other parameters analysed.

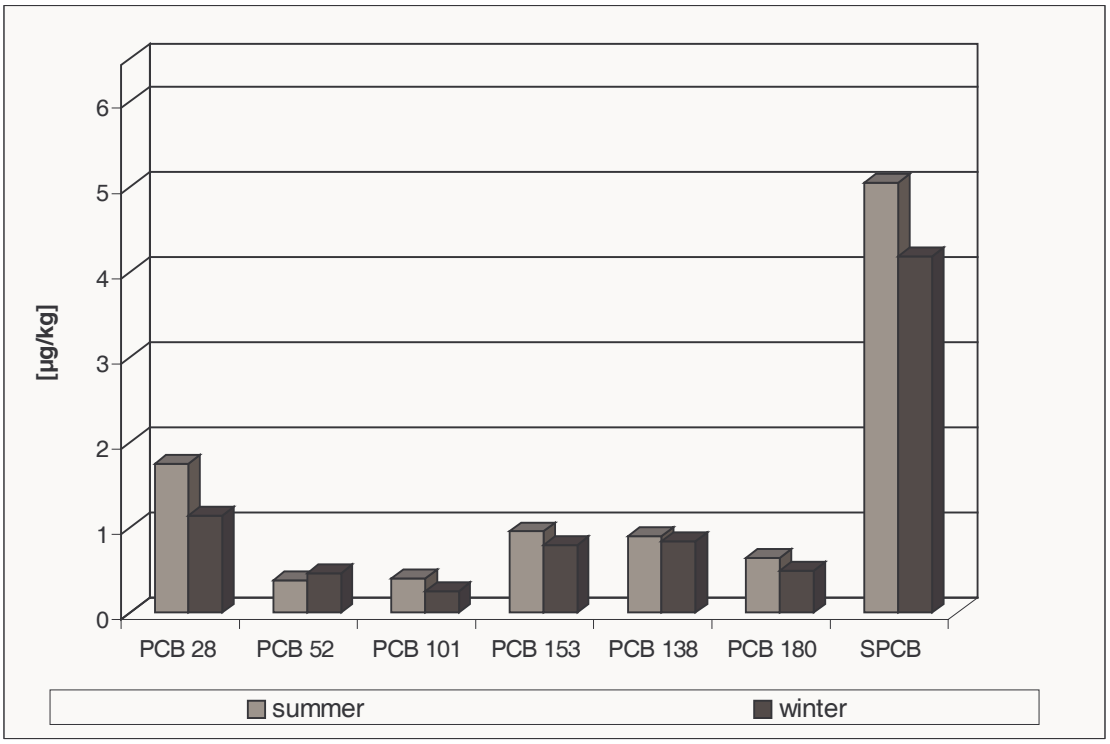

Figure 3.19. Individual distribution of PCB and their summation (SPCB) for Seil Zarqa tributary (Z1-Z10).

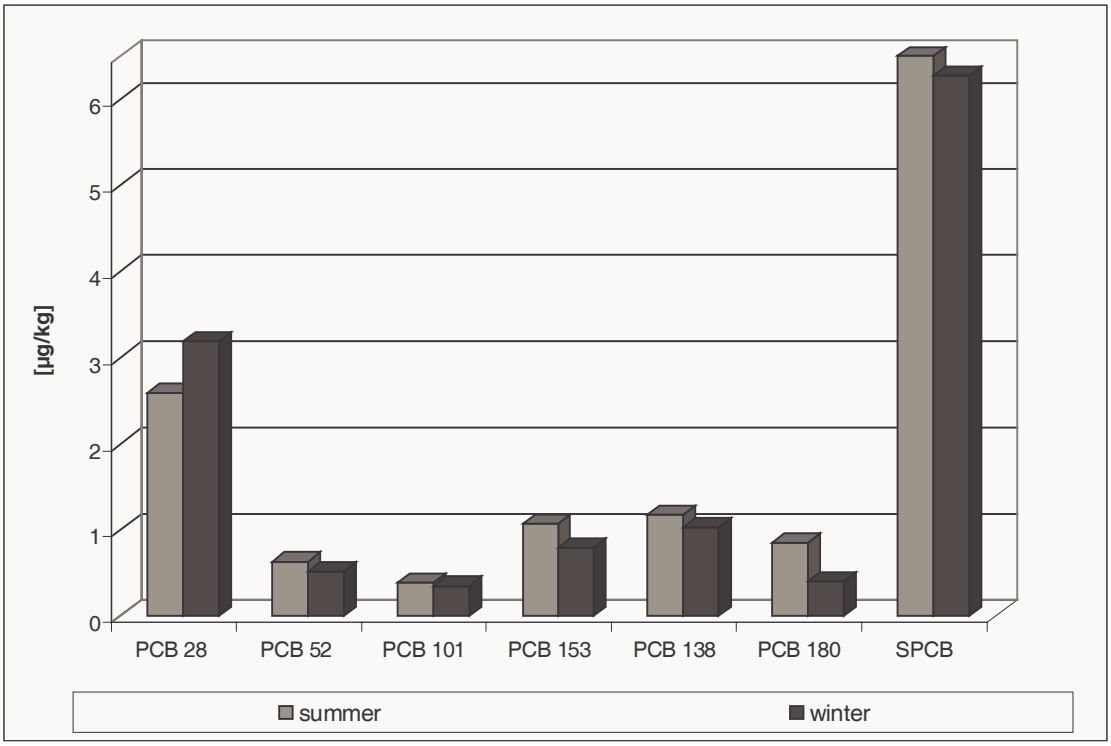

Figure 3.20. Individual distribution of PCB and their summation (SPCB) for Wadi Dhuleil tributary (D1-D4).

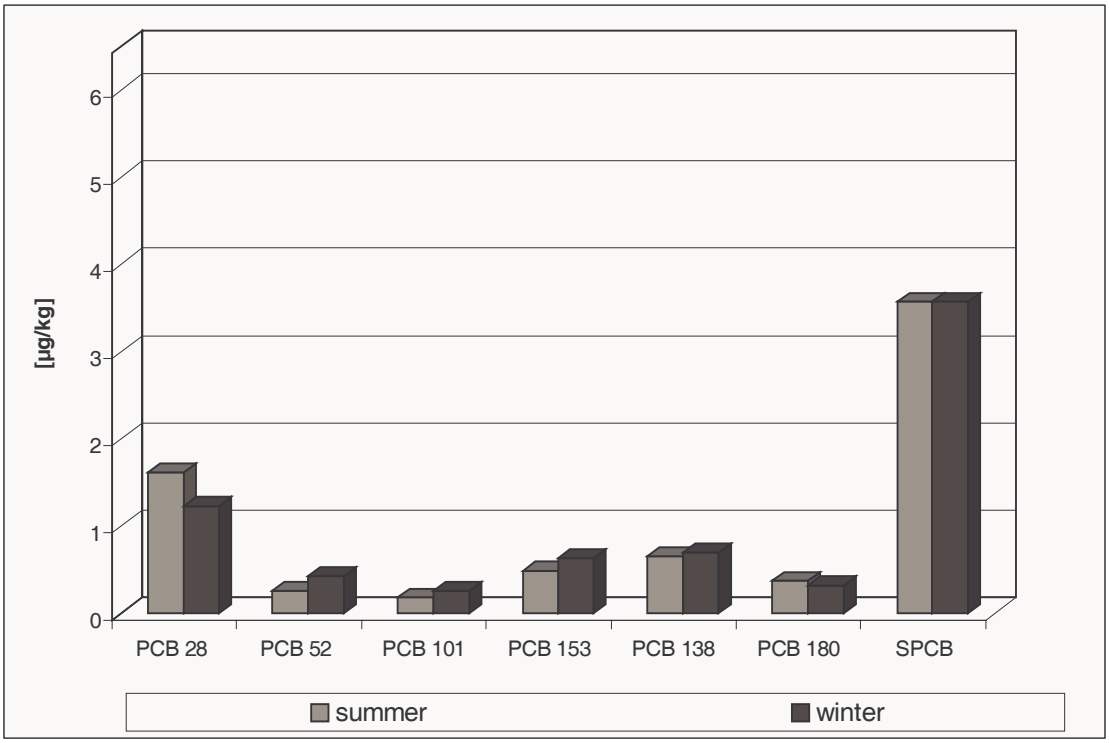

Figure 3.21. Individual distribution of PCB and their summation (SPCB) for Zarqa River (R1-R4).

3.7.2 Trends of PCB and PAH

The following trends can be concluded by comparing PCB and PAH concentrations among all samples. Firstly, similar PAH and PCB trends were observed along Seil Zarqa tributary in summer season. Especially, from sites Z1 to Z5, the PCB and PAH concentrations are steadily increased. For winter season, a significant correlation coefficient (R^2= 0.85) was obtained between PCB and PAH concentrations for the samples from WZ1-WZ10. In addition, similar trends of PCB and PAH were noticed along sampling sites R1-R4, with correlation coefficients of 0.69 and 0.72 for summer and winter seasons, respectively. However, Wadi Dhuleil has shown relatively different PCB and PAH trends because of the samples heterogeneity. The line graphics are used to present the total concentration trends of PCB and PAH for both sampling periods **figures 3.22** and **3.23**.

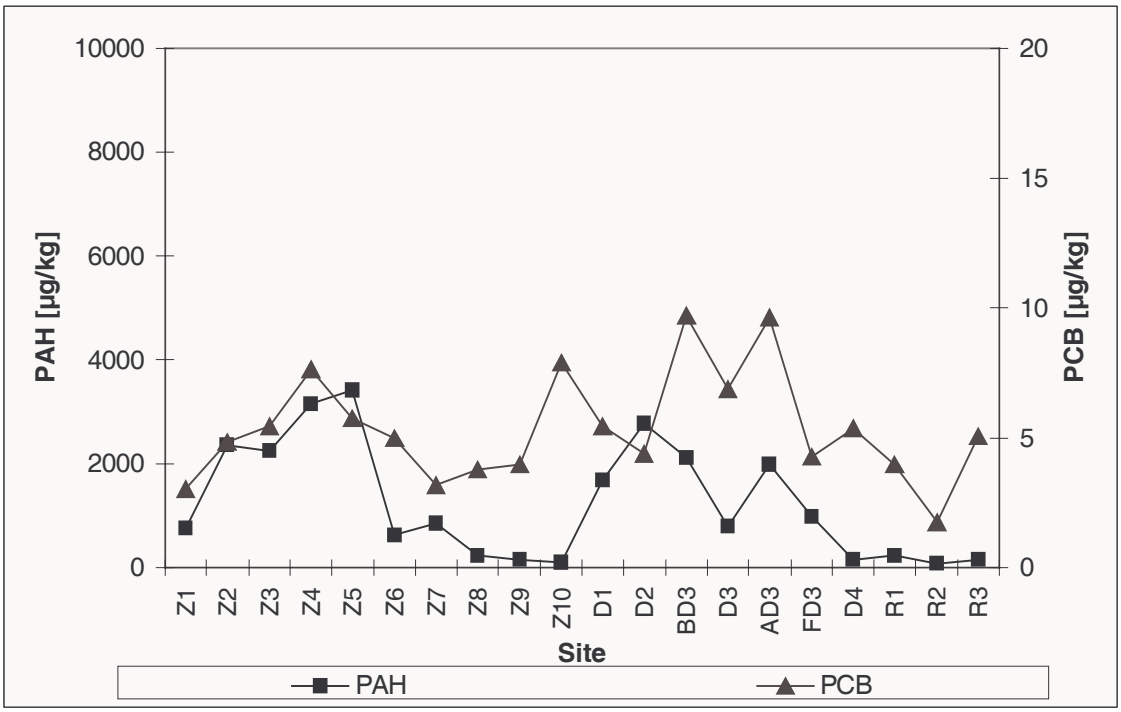

Figure 3.22. PCB and PAH distribution trends in summer seasons.

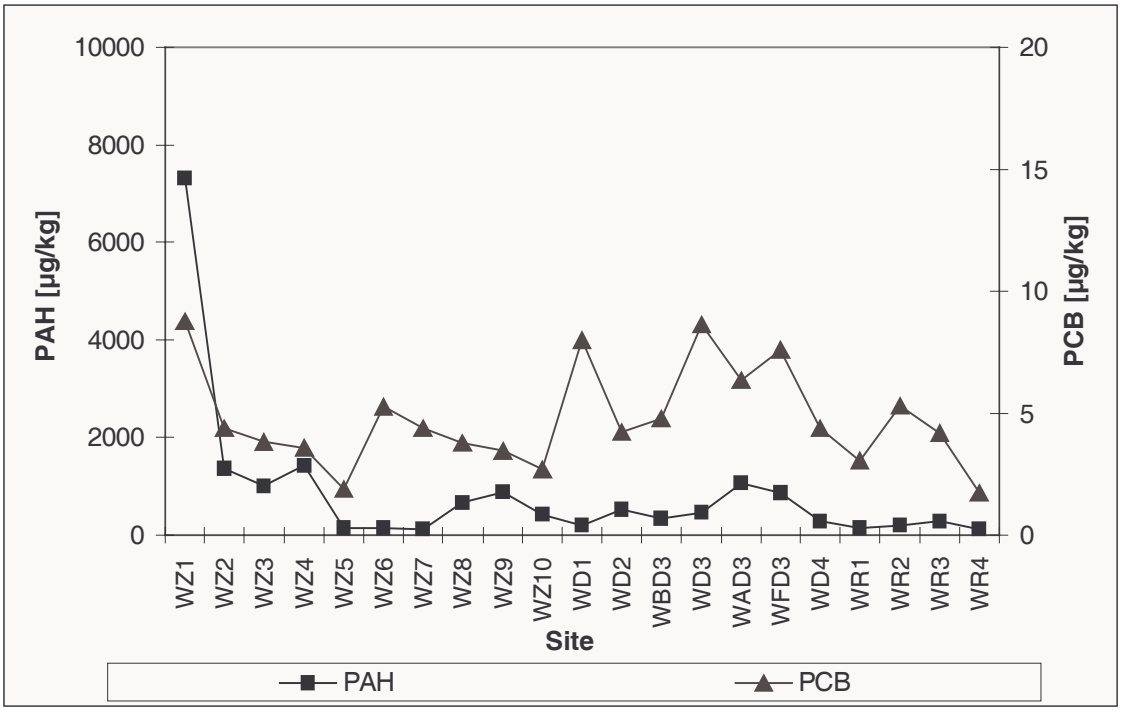

Figure 3.23. PCB and PAH distribution trends in winter seasons.

3.7.3 PCB findings from different countries

Concentration of PCB congeners in sediments from the literature for different countries compared to the present work findings are presented in **table 3.12**. The overall PCB concentration for the present work ranged over 0.37-31.12 µg/kg on dry weight basis which were much lower than those concentrations obtained at industrialized countries. For example in Germany at Elbe River the total PCB concentration in sediments was found by factor about 10 greater than in the present work, in Netherlands at River Rhine which passes five countries they ranged from 50 to 670 µg/kg on dry weight basis, and in Canada at St. Lawrence River the ΣPCB ranged from 158 to 347 µg/kg d.w. However, lower concentrations of PCB congeners were found at Yangtse River in China (0.39-1.13µg/kg d.w.). Finally, same levels of PCB concentrations were obtained at Ebro River in Spain (14.13 µg/kg d.w.) compared to the present work .

The total PCB congeners concentration is set for sewage sludge for agricultural use in European Union as 0.8 mg/kg on dry weight basis (EU, 2000), and in Germany as 0.2 mg/kg on dry weight basis (UBA, 1992). Switzerland set the total concentration of 7 IUPAC PCB isomers for soil as 0.005 mg/kg of dry soil (DSBR, 1998). In addition, EPA's guideline value for bioaccumulation of PCB in living organsims for ocean placement is 113 ppb (µg/L) (US-EPA, 2000).

Table 3.12. Average concentrations or ranges of PCB in µg/kg dry weight detected in sediments from different countries.

Site/Country	ΣPCB	Reference
Elbe River/Magdeburg/Germany	109	Kolb, 1994
River Rhine/Netherlands	50-670	Evers et al., 1988
St. Lawrence River/Canada	158-347	Coakley et al., 1993
Ebro River (Spain)	14.13	Fernández,1999
Yangtse River (China)	0.39-1.13	Xu et al., 2000
Present work (December, 2000)	0.37-31.12	-
Present work (November, 2001)	1.72-9.69	-
Present work (January, 2002)	1.73-8.77	-

3.8 Organochlorine pesticides

Results given in **tables 5** and **6** in **appendix** present the concentration levels of 12 organochlorine insecticides in sediment samples collected during November 2001 and January 2002. The analytical repeatability of the results expressed as relative standard deviation (RSD) were generally less than 20 %. However, β-HCH, δ–HCH and heptachlor made an exception, they showed high RSD values in winter season because of matrix interferences at low concentrations. More details are discussed in sections 3.2.5.

Generally, high concentration variability of all target organochlorine insecticides and relative compounds were found in sediments. Higher concentration levels were obtained for summer sampling period than in winter. The predominant organochlorine compounds were DDT metabolites and hexachlorocyclohexane isomers, whereas, cyclodienes were detected in low concentration levels and occasionally. In fact, DDTm were present in 80 % of all summer samples and in 76 % of winter. HCH isomers were present in 42 % for summer samples and 34 % for winter samples. However, only 15 % and 8 % of cyclodiens were detected in summer and winter samples, respectively. The distribution pattern of organochloine compounds are classified into three groups: DDT metabolites, HCH isomers and the cyclodiene group. In order to get better understanding of the distribution pattern and occurrence, they are discussed in the following sections separately.

3.8.1 Distribution pattern of DDT metabolites (DDTm)

The metabolism of DDT through dehydrochlorination to DDE and reductive dechlorination to DDD are the most important transformations of DDT which are usually studied and detected in the environment (Strandberg, 2000; Spiro and Stigliani, 1996). The DDT metabolites showed the highest concentration levels among the 12 investigated insecticides and relative compounds. The distribution pattern as total DDTm in µg/kg on dry weight basis for summer and winter sampling periods are presented in **figure 3.24**. Generally, 2-15 times higher concentration levels of DDTm were found for summer than in winter sampling period. The total concentrations of DDTm ranged over 3.6-125.8 ± 39.2 µg/kg with average 39.7 µg/kg for summer season, and to 2.1-46.4 ± 10.8 µg/kg with average 16.3 µg/kg for winter season. The maximum concentrations of total DDTm were determined at sites BD3 (125.8 µg/kg

d.w.) and WD3 (46.4 µg/kg d.w.) for summer and winter seasons, respectively. The minimum concentrations were found at sites Z9 (3.6 µg/kg) and WZ7 (2.1 µg/kg). Wadi Dhuleil contained the highest levels of DDT metabolites, while lower levels were obtained for Seil Zarqa and down stream of Zarqa River. The average concentrations of total DDT metabolites were 18.7, 81.2 and 13.2 µg/kg d.w. for summer season, and 15.6, 20.4 and 9.4 µg/kg d.w. for winter season, for Seil Zarqa, Wadi Dhuleil and Zarqa River categories, respectively.

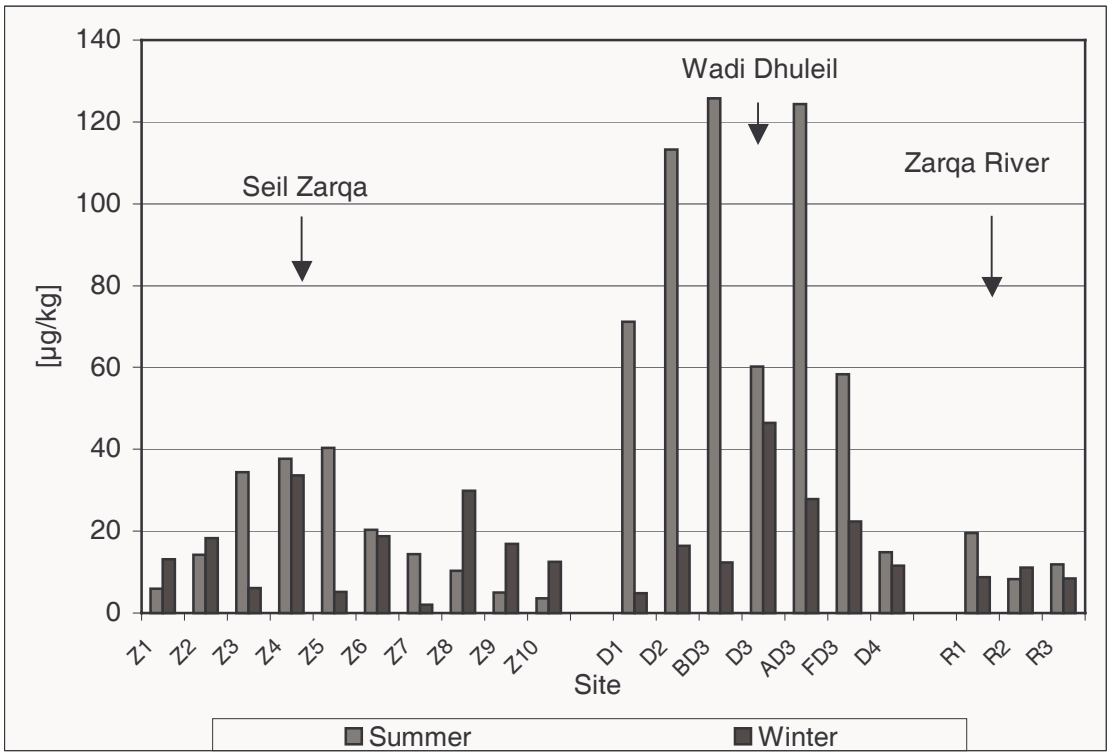

Figure 3.24. Distribution pattern for summation of four DDT metabolites in µg/kg dry weight in sediment for summer and winter seasons.

The findings of the present work for DDT metabolites were found in agreement with those of Alawi et al. (1995). They had investigated levels of organochlorine pesticides in fish, algae, sediments, and sea water. They have concluded that most of the investigated samples were contaminated with p,p´-DDT and p,p´-DDE. For example, the average concentration of p,p´-DDE were found 11.46, 8.07, 0.07 µg/kg and 0.18 µg/L in fish, algae, deep sediments and sea water from Aqaba Gulf, respectively. In addition, Al-Mughrabi and Qrunfleh (2002) had investigated the pesticides residues in soils from Jordan Valley. They found that p,p´-DDE (0.04-0.46 mg/kg) and p,p´-DDD (0.04-0.16 mg/kg) were the dominant species, while p,p´-DDT appeared at the highest

concentration (4.05 mg/kg). However, DDT was banned from agricultural uses in Jordan since 1980, but it is still used in recent years for health protection purposes. Significant correlations were observed between total concentrations of DDT metabolites and the total organic matter for both sampling periods. The correlation coefficients were: 0.90, 0.59 and 0.85 for summer season and 0.12, 0.96 and 0.88 for Seil Zarqa, Wadi Dhuleil and Zarqa River categories, respectively.

3.8.2 Distribution pattern of HCH isomers

The technical mixture of hexachlorcyclohexane (HCH) is composed of four isomers (α,β,γ and δ), however, γ-HCH is 50-10000 times as active as the α and δ isomers, while β-HCH is inactive. The composition of the technical HCH according to Slade in 1945 are: up to 70 % α-HCH, 5 % β-HCH,10-12 % γ-HCH and 7 % δ-HCH (Matolcsy, 1988). The distribution trends of the total concentrations of hexachlorocyclohexane isomers (ΣHCH) for both sampling periods are presented in **figure 3.25**. Summer season reported higher concentration levels than winter season and Seil Zarqa shown higher concentration levels than Wadi Dhuleil and Zarqa River. The ΣHCH on dry weight basis ranged over 0.8-11.5 ± 2.9 µg/kg with an average 4.6 µg/kg for summer and 0.8-16.0 ± 3.5 µg/kg with an average 3.4 µg/kg for winter. The maximum concentrations were determined at sites Z7 (11.5 µg/kg) and WZ1 (16.0 µg/kg) for summer and winter seasons, respectively. However, minimum concentration (0.8 µg/kg) was found down stream of Zarqa River at sites R1 and WR3. The wide range variation of HCH concentration might be explained due to four factors: heterogeneity of the sample matrix, type of activities nearby sampling site, time of pesticides application, as the fourth one the chemical and physical insecticide properties are responsible for its behavior under different environmental conditions.

A significant correlation was observed between total concentrations of HCH and TOC in winter season. The correlation coefficients were: 0.88, 0.65, and 0.67 for Z, D, and R categories, respectively, while, no correlation were obtained in summer season. In addition, some correlations were observed between ΣHCH and sediments particles fractions. For summer, categories Z and R significantly correlated to the clay fraction. The correlation coefficients were 0.95 and 0.91. However, weak correlation was observed for winter season.

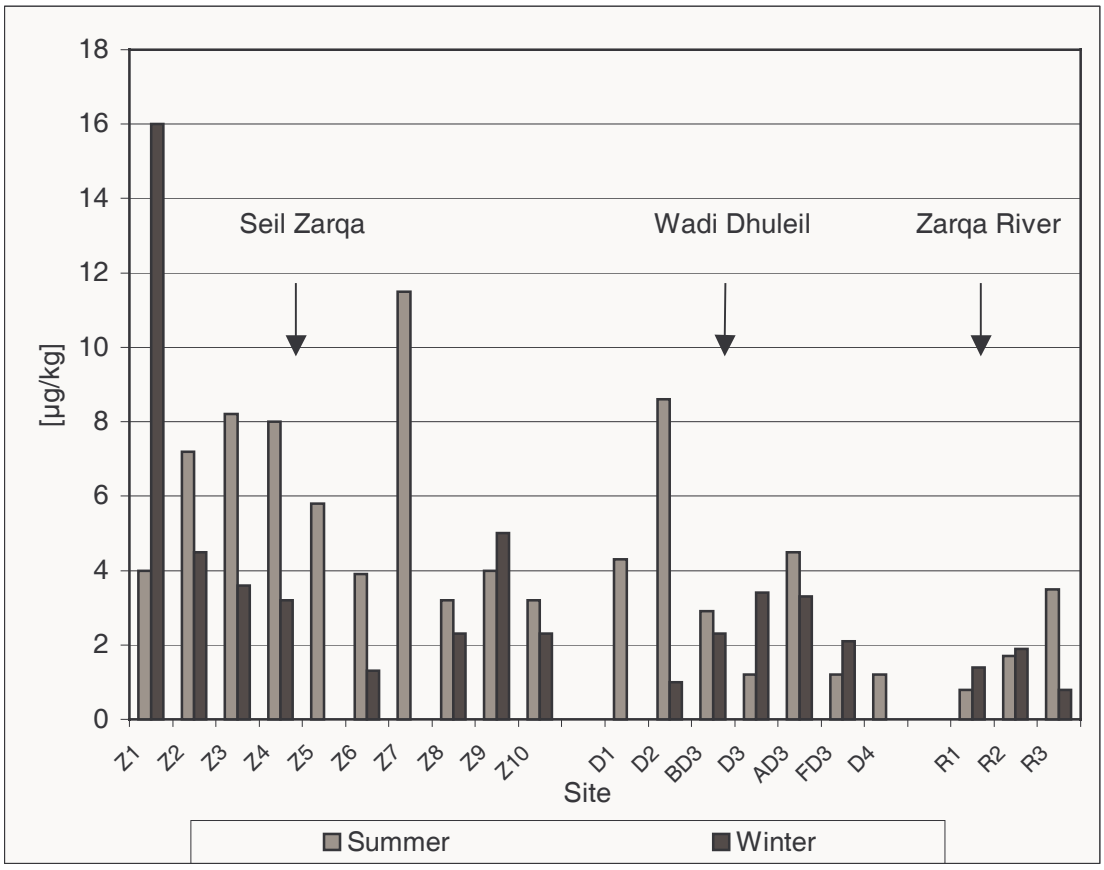

Figure 3.25. Distribution pattern of summation of four hexachlorocyclohexane isomers (ΣHCH) in µg/kg dry weight in sediment for summer and winter seasons.

The presence of detectable concentrations of hexachlorocyclohexane isomers can only be interpreted as the residues of large amounts of lindane which had been applied in the area or this insecticide is still used in Jordan for public health purposes. Furthemore, hexachlorocyclohexanes are still used in veterinary medicine in Jordan (Nasir et al., 1998). The findings of the present work agreed with the previous studies for HCH residues in Jordanian environment. For example, environmental relevant concentrations of α-HCH (0.02-0.14 mg/kg) were found in soil from Jordan Valley (Al-Mughrabi and Qrunfleh, 2002). α-HCH (0.18 mg/kg fat and 0.04 mg/L milk) and γ-HCH (0.71 mg/kg fat and 0.11 mg/L milk) were detected in human milk of Jordanian women (Nasir et al., 1998). β-HCH was detected in Jordanian human adipose tissues which was found as 1.13 and 0.59 µg/g lipid for smoker and non-smoker tissues, respectively (Alawi and Ababhneh, 1991). In addition, α–,β– and γ-HCH were determined as sum of average of three isomers as 18.43, 4.47, 0.03 µg/kg and 0.21 µg/L in fish, algae, sediments and sea water in Aqaba Gulf, respectively (Alawi et al., 1995).

3.8.3 Individual distribution of DDTm and HCH

The concentrations of individual organochlorine insecticides and their related compounds varied widely. The individual distribution pattern of DDTm and HCH are presented for each sampling category in **figures 3.26**, **3.27** and **3.28**. The cyclodienes were excluded from graphical presentation because they were uniquely detected. The predominant DDTm were p,p´-DDD > p,p´-DDE > o,p-DDD > o,p-DDE and their average concentrations: 8.62, 7.78, 19.17 and 11.18 µg/kg d.w. for summer and 3.52, 5.08, 6.16 and 5.73 µg/kg d.w. for winter. The highest average concentration was found at Wadi Dhuleil (40.8 µg/kg d.w.) for o,p´-DDD and the lowest for p,p´-DDE (1.4 µg/kg d.w.) down stream of Zarqa River for summer season. However, in winter season the highest and lowest average concentrations were found at the same sites like in summer, they were for p,p´-DDD (8.4 µg/kg) and o,p-DDD (2.8 µg/kg), respectively. The incident ratios of DDTm in analyzed samples are summarized in **table 3.13**.

Table 3.13. The incident ratios of DDTm in analyzed samples.

Compound	Summer [%]	Winter [%]
o,p-DDE	55	43
p,p´-DDE	80	71
o,p-DDD	85	86
p,p´-DDD	100	86

The analytical findings showed that α-HCH and β-HCH were the predominant isomers, while, γ-HCH and δ-HCH isomers detected in traces. The incident ratios for α–,β–,γ– and δ–HCH isomers consequently were: 90, 30, 25 and 25 % for summer, and 62, 52, 5 and 10 % for winter sampling period. The average concentrations on dry weight basis of α-, β-, γ-, and δ-HCH were 3.13, 1.97, 2.00 and 1.78 µg/kg for summer, and 2.38, 1.68, 2.60, and 1.15 µg/kg for winter, respectively. The highest average concentrations of HCH were found for γ-HCH (5.10 µg/kg) at Wadi Dhuleil for summer season and for α-HCH (3.60 µg/kg) at Seil Zarqa for winter. Whereas, lowest concentrations were recorded down stream of Zarqa River for α-HCH (0.80 and 1.00 µg/kg d.w.) for both seasons.

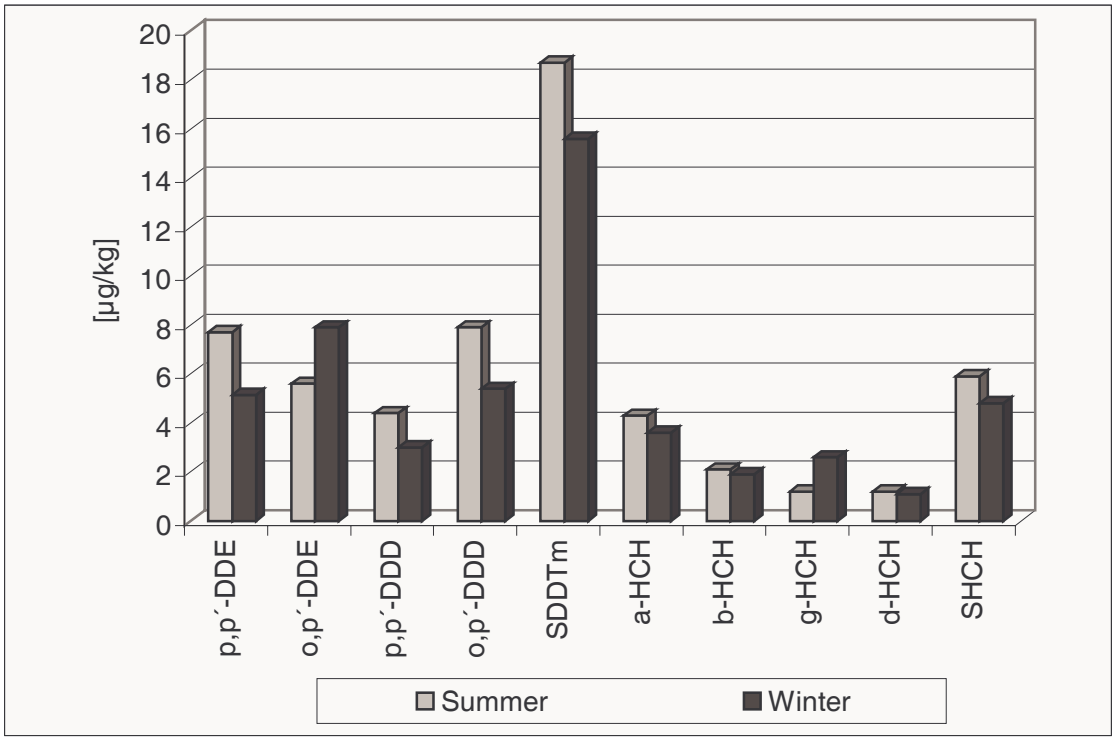

Figure 3.26. Individual distribution of mean concentrations of DDTm and HCH and their summation (SDDTm, SHCH) for Seil Zarqa (Z1-Z10).

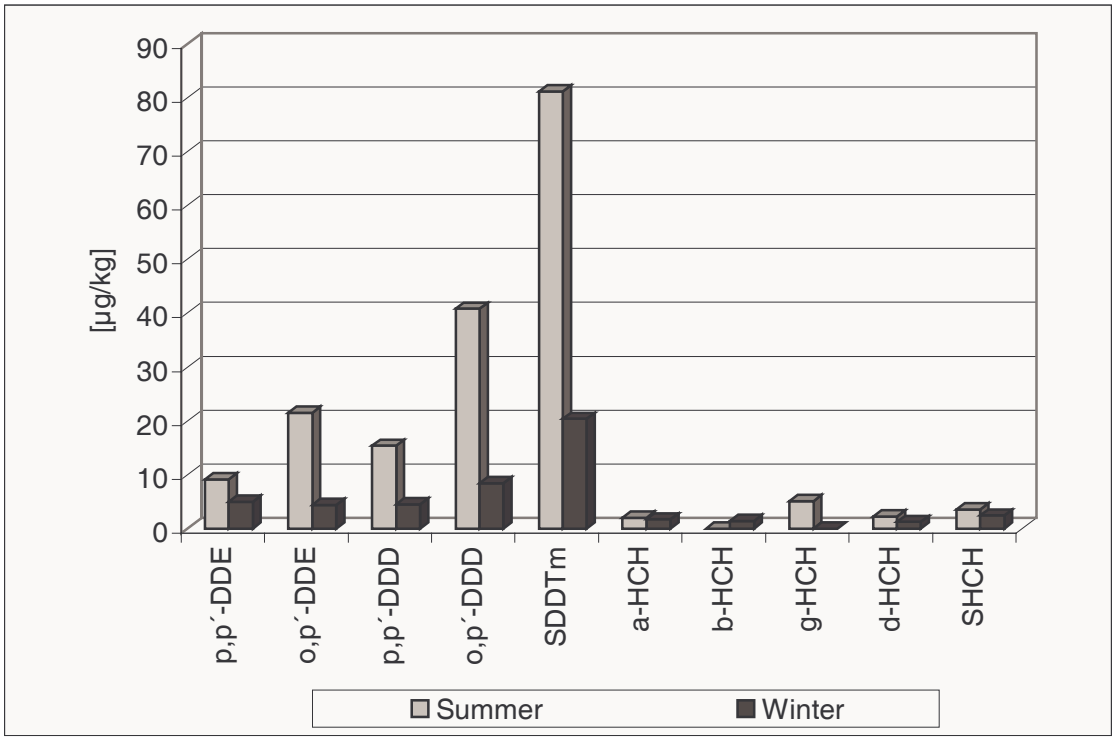

Figure 3.27. Individual distribution of mean concentrations of DDTm and HCH and their summation (SDDTm, SHCH)for Wadi Dhuleil (D1-D4).

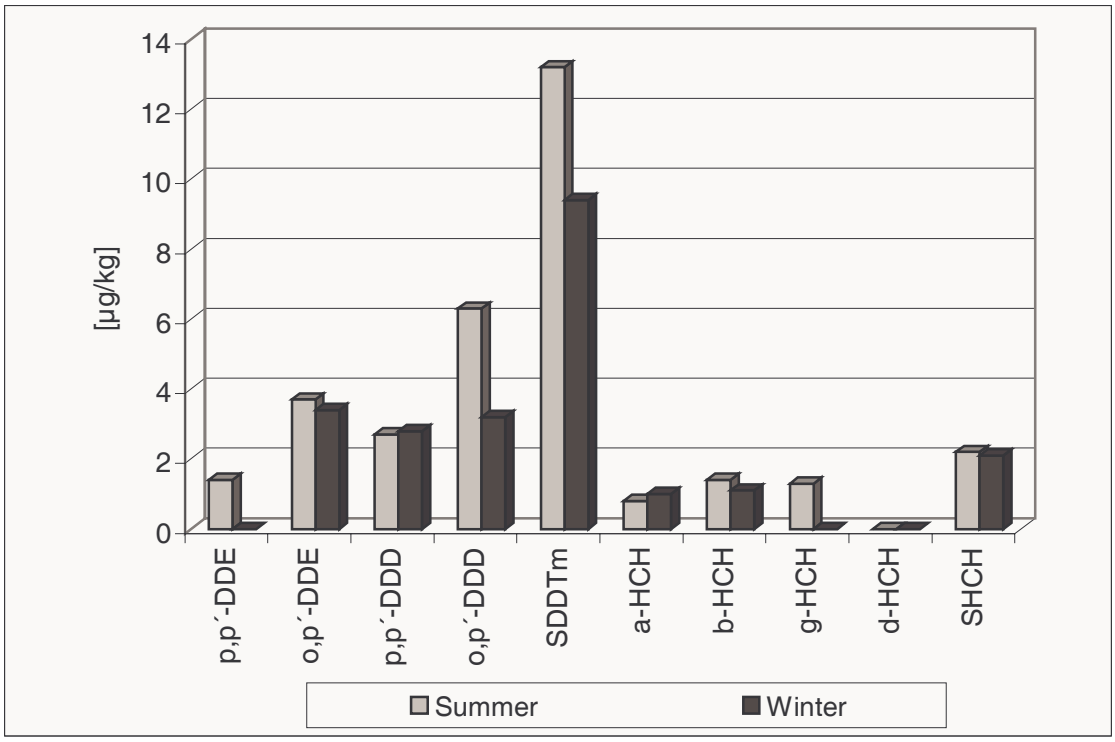

Figure 3.28. Individual distribution of mean concentrations of DDTm and HCH and their summation (SDDTm, SHCH) for Zarqa River (R1-R4).

3.8.4 Distribution pattern of cyclodienes

Heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide and dieldrin were investigated in the present work among the cyclodiene insecticides. Heptachlor and its metabolites were uniquely detected in most of samples. However, dieldrin was the dominant insecticide and it was detected in 70 % of the summer samples but only in 10 % of the winter. Its concentration on dry weight basis ranged from 1.3 to 84.5 µg/kg for summer and from 1.8 to 9.6 µg/kg for winter. The maximum concentrations were found at sites FD3 (84.5 µg/kg) and WZ1 (9.6 µg/kg). These findings might be explained according to the fact that they are no longer used as insecticides in Jordan and only residues are still detected in Jordanian environment. Another possibility is some of these cyclodiene insecticides are still used without knowledge or illegally. No correlation is obtained between the total concentrations of cyclodienes and the organic matter content for summer. While, categories Z and R obtained significant correlations for winter sampling period.

Alawi et al. (1995) have reported low concentrations of heptachlor (0.168-1.272 µg/kg) and dieldrin (0.096 µg/kg) in Aqaba Gulf sediments. In addition to heptachlor epoxide,

all were detected in higher concentration levels in fish (heptachlor: 2.38 µg/kg, heptachlorepoxide: 2.42 µg/kg, dieldrin: 12.02 µg/kg), algae (heptachlor: 4.91 µg/kg, heptachlorepoxide: 5.00 µg/kg, dieldrin: 12.19 µk/kg) and in water (heptachlor: 0.022 µg/L, heptachlorepoxide: 0.034µg/L, dieldrin:0.050 µg/L). Al-Mughrabi and Qrunfleh, (2002) have detected dieldrin (0.09 mg/kg) in Jordanian soils from Jordan Valley. Furthermore, the target cyclodienes were found to occur in Jordanian human milk (heptachlor: 0.50 mg/kg fat and 0.07 mg/L milk , heptachlor epoxide: 0.19 mg/kg fat and 0.05 mg/L milk, dieldrin: 1.41 mg/kg fat and 0.66 mg/L milk) (Nasir et al., 1998), as well as in non-smoker adipose tissue (heptachlor: 0.42 µg/g lipid, heptachlorepoxide: 7.55 µg/g lipid, dieldrine: 0.34 µg/g lipid) (Alawi and Ababneh, 1991).

3.9 Chlorobenzenes (CBz)

Hexachlorobenzene (HCBz) and pentachlorobenzene (PCBz) were investigated in the present work because of their relative stability comparing with other CBz. The analytical method has shown poor recovery for more volatile CBz. The concentrations of HCBz and PCBz are listed in **tables 3** and **4** in the **appendix** for summer and winter seasons, respectively. They were analyzed together with PCB in the same silica gel fraction and under the same chromatographic conditions. The repeatability of the results was acceptable (RSD < 20 %) for summer season, whereas, for winter season PCBz was not detected in the repeated samples and HCBz was detected in very low concentration. More details are discussed in sections 3.2.4 and 3.2.5. The recovery rate of HCBz ranged from 70 to 81% and of PCBz from 52 to 59 %, where the low recovery rate of PCBz was because of its high volatility.

PCBz was presented in about 60 % of the samples analyzed for both sampling periods. Its distribution pattern is illustrated in **figure 3.29**. The concentrations of PCBz ranged over 0.13-0.58 ± 0.15 µg/kg with an average 0.29 µg/kg for summer, and 0.07-0.74 ± 0.20 µg/kg with an average 0.21 µg/kg on dry weight basis for winter. The maximum concentration of PCBz was found at sites R2 (0.58 µg/kg) and WAD3 (0.74 µg/kg), however, the minimum concentration was found at sites Z2 and Z8 (0.13 µg/kg) for summer and at more than three sites (0.07 µg/kg) for winter. Some significant correlations were observed between the concentrations of PCBz and the organic matter. The correlation coefficients for Z, D, and R categories were respectively 0.82, 0.66, and –0.69 for summer, and 0.65, 0.28 and 0.52 for winter samples.

The distribution pattern of HCBz for both sampling periods is presented in **figure 3.30**. The concentration of HCBz ranged over 0.13-3.34 ± 0.78 µg/kg with an average 0.97 µg/kg and 0.07-1.51 ± 0.40 µg/kg with an average 0.56 µg/kg on dry weight basis for summer and winter sampling periods, respectively. The concentration levels of HCBz for summer was approximately doubled than in winter one. The highest HCBz concentration was determined at sites Z4 (3.34 µg/kg) for summer and WZ1 (1.51 µg/kg) for winter. Mostly, HCBz concentrations were significantly correlated to the organic matter content. The correlation coefficients for Z, D, and R categories were respectively 0.67, 0.27, and 0.73 for summer, and 0.58, 0.91, and 0.67 for winter samples.

The sources of CBz in the studied area might be originated from the practices of the industrial waste disposal and using HCBz as fungicide in agricultural filed. HCBz has been ranged from 0.048 to 0.192 µg/kg d.w. in sediments from Aqaba Gulf but the highest average concentration was found in fish (3.02 µg/kg) (Alawi et a.,1995). In addition, it was determined in Jordanian soil as 0.04 mg/kg (Al-Mughrabi and Qrunfleh, 2002). However, no data is available explaining the occurrences of PCBz in Jordanian environment.

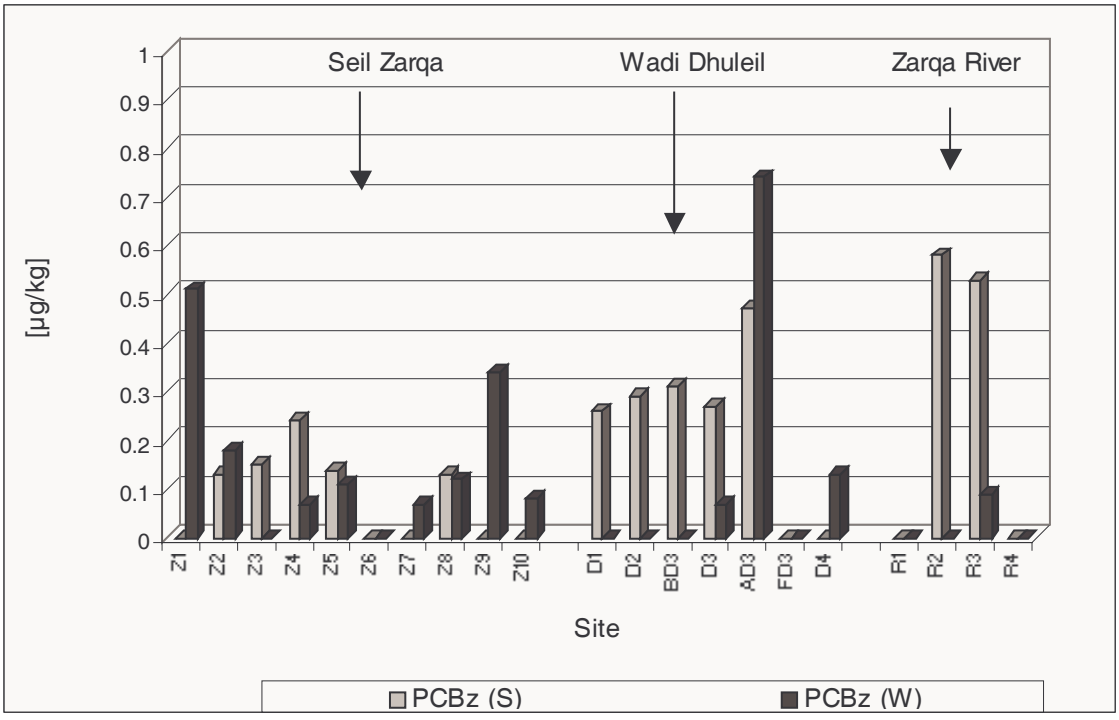

Figure 3.29 Distribution pattern of PCBz in µg/kg dry weight in sediment for summer (S) and winter seasons (W).

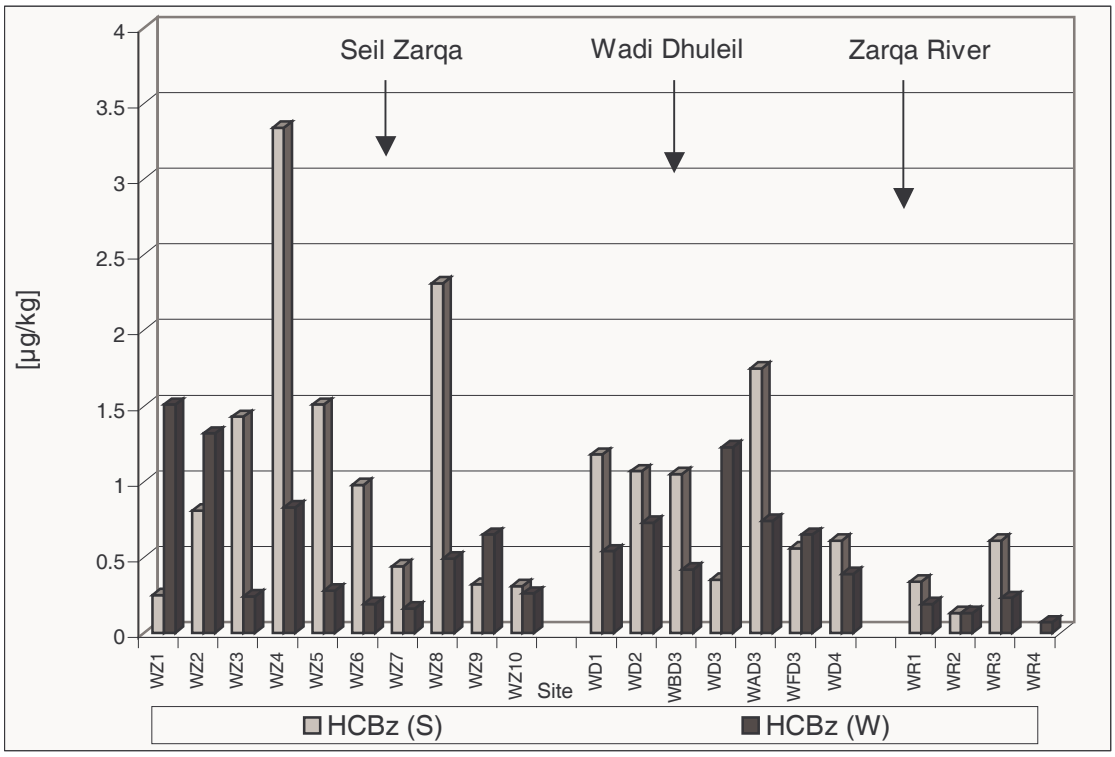

Figure 3.30. Distribution pattern of HCBz in µg/kg dry weight in sediment for summer (S) and winter seasons (W).

3.10 Organochlorine pesticide's concentration from different countries

Concentrations of organochlorine pesticides in µg/kg on dry weight basis in sediment are collected from the literature for different countries and compared to the present work. They are listed in **table 3.14**. The ΣDDT and its metabolites in the present work were observed to have approximately the same concentration levels as in the Indian marine sediments, but found to be 2-4 times more than those concentrations which found in Egypt at Nile Delta. In addition, these values of ΣDDTm are much greater than those concentrations measured at Shatt al-Arab River in Iraq, Epirus in Greece and at Elbe River in Germany. However, the image is reflected for ΣHCH, they were determined in higher concentration levels at Elbe River by factor of about 300 times higher than in the present work and by factor about 22 was found at Köyceğiz Lagoon system in Turkey. Furthermore, ΣHCH were found in much higher concentration levels at Nile Delta and at Alibagh in India, but lower concentration was obtained at Epirus as only lindane (γ-HCH).

Table 3.14. Concentrations of selected organochlorine pesticides [µg/kg d.w.] in sediments from different countries.

Site/Country	ΣDDT	ΣHCH	HCBz	Cyclodienes	Reference
Shatt al-Arab River/Iraq	5.0	-	-	20 (Dieldrin)	Douabul et al., 1987
Epirus /Greece	0.1-21.6 (DDE)	0.1-0.5 (γ-HCH)	0.1-0.5	0.1-1.6	Piperidou et al., 1994
Greenland	-	-	<DL (0.02-0.12)	-	Fromberg et al., 1999
Köyceğiz Lagoon/Turkey	-	1-411	-	20-87	Yerli and Caliskan,1997
Elbe River / Magdeburg Germany	25.0 (p,p´-DDE)	3606	606.0	-	Kolb, 1994; Oxynos et al., 1995
Kaohsiung coast/Taiwan	-	-	0.1-61.6	-	Lee et al., 2000
Nile Delta/ Egypt	0.6-29.6	4.1-52.3	-	0.9-68.0	Abd-Alla et al., 1992
Alibagh / India (1995)	2.0-71.9	11.7-108.1	-	-	Pandit et al., 2001
Present work (Summer, 2001)	3.6-125.8	1.2-11.5	0.13-3.34	1.3-84.5	-
Present work (Winter, 2002)	2.1-46.4	0.8-16.0	0.07-1.51	1.5-13.4	-

Similar concentration levels of HCBz were found for the present work compared to those obtained in Greece and Greenland, while higher concentration by factor of about 240 determined at Elbe River in Germany and by factor about 25 at Kaohsiung coast in Taiwan. Overall, relatively close concentration levels for cyclodienes to those obtained in the present work were found at Shatt al-Arab River in Iraq and in Egypt at Nile Delta. Total concentration of cyclodienes were appeared mostly at the same levels for most of cited sites, however, lower levels was observed at Epirus in Greece.

4. Summary

Environmental analysis and monitoring study were performed for Zarqa River basin. It was aimed to evaluate the environmental quality and to measure the environmental background concentrations of a group of selected semivolatile organic pollutants as well as studying their distribution pattern during the seasonal variation.

An analytical method was developed for the residue analysis of polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorinated benzenes (CBz) and organochlorine pesticides (OCP) in sediments which were heavily loaded with sewage wastewater. The analytical protocol includes column extraction and sophisticated clean up procedures. The target compounds were separated into two fractions using silica gel column chromatography. The first fraction included PCB and CBz analyzed by GC/ECD and the second fraction for PAH and OCP using GC/MS and GC/ECD, respectively.

The analytical method enables the quantification of these pollutants in sediments at concentrations which were determined on dry weight basis as low as 0.12 µg/kg for PCB, 0.07 µg/kg for CBz, 0.98 µg/kg for OCP, and 1.0 µg/kg for PAH. The quality assurance measurements were carried out firstly to evaluate the precision of the analytical method and to determine its limit of determination (LOD). Secondly, to determine the detection limit (DL) and instrument detection limit (IDL) based on signal to noise ratio (3:1). Finally, confirmation of the GC/ECD and total organic carbon (TOC) results were performed in addition to quality assurance of the sampling storage and ageing effects on concentration of organic pollutants in sediment. Totally, the sampling activities were carried out during the periods of December 2000 and from November 2001 to January 2002.

Generally, higher contamination levels along Zarqa River sediments were found compared to those obtained at the reference site. The major parameters that determine the contamination levels are likely to be the type of the anthropogenic activity, the distance from the pollution source, physical and chemical properties of the sediment, and rainfall quantities which might control the transport of the sediments along the river discharge system. The direct discharge of the low quality treated wastewater and untreated industrial and domestic wastewater discharge clearly affected the quality of the sediments. As consequences, high concentration levels of organic matter were

found, they ranged to 1.43-28.09 with an average 10.33 % for summer, and to 0.70 to 34.70 with an average 6.08 % for winter. The variability of organic matter content is dependent mainly on location of the point source of wastewater effluent or waste disposal and on the rainfall quantities. The highest contamination levels were found nearby As-Samra wastewater effluents at Wadi Dhuleil.

The distribution pattern and concentration levels of PAH in sediments were strongly dependent on organic matter content. The summer sampling period has shown higher concentrations of the sum of 16 PAH than for winter. In addition, lower concentration levels of PAH were detected down stream of Zarqa River than up stream. The sum concentrations of 16 PAH on dry weight basis (d.w.) ranged to 69-3414 µg/kg for summer and 111-1419 µg/kg for winter. At site WZ1 extreme PAH concentration appeared and excluded from calculation. The distribution pattern of PAH and their profiles have explained the PAH accumulation and sources in the studied area, which depended on the direct influence of the anthropogenic activities, type and amount of wash out processes and direction of water flow.

The distribution pattern of PCB for both sampling periods were similar and their concentrations significantly correlated to the sediment organic matter. The sum of 6 PCB congeners ranged to 1.72 to 9.69 µg/kg d.w. Particularly, the PCB showed a similar distribution pattern to the PAH along the sampling sites and their concentrations significantly correlated. The studied area was low contaminated with PCB congeners comparing with concentration levels for other countries. The permanent industrial waste disposal or discharges into the aquatic environment via As-Samra WSPs or by direct discharge into the river drainage system might be the main sources of PCB pollution in Zarqa River sediments.

The chlorobenzenes were detected in low concentrations. The concentrations ranged to 0.13-0.53 µg/kg d.w. for PCBz and 0.13-3.34 µg/kg d.w. for HCBz in summer. In winter, PCBz ranged to 0.07-0.74 µg/kg d.w. and HCBz to 0.07-1.51 µg/kg d.w. The concentrations of CBz significantly correlated to the sediment organic matter. Similar concentration levels of HCBz were found for the present work compared to those obtained in Greece and Greenland, while greater concentration were observed in industrialized countries, for example it was found at Elbe River in Germany by factor 240 higher than at Zarqa River sediments.

12 organochlorine pesticides were investigated in the present work. The Zarqa River sediment was highly contaminated with some organochlorine pesticides residues which were dominated by DDT metabolites. Higher concentration levels of four DDTm were detected in summer than in winter. They ranged to 3.6-125.8 µg/kg for summer and 2.1-46.4 µg/kg for winter. However, lower contamination levels were observed with hexachlorocyclohexane isomers and cyclodienes. Nevertheless, the irregular distribution of these pollutants along sampling sites might be explained due to the way of input into the river drainage system and the application time as well as the heterogeneity of the sample matrix.

The Jordanian ecosystem studied was found less contaminated with polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), chlorobenzenes (CBz) and part of organochlorine pesticides residues than other urbanized and industrialized countries in Europe as well as north America. For example higher concentration levels of most target compounds were found in Germany, Canada, and Netherlands than obtained in the present work.

Totally, the discharge of organic load from domestic and industrial wastewater and waste disposals into Zarqa River have led to an environmentally elevated concentrations of organic pollutants in the river sediments. A site control in a combination with the present work provides a better information and understanding of the chemical contamination and may facilitate the interpretation of data. Further studies concerning behavior and distribution of organic pollutants at source pollution sites as well as surface water, groundwater, soil and cultivated crops along Zarqa River should be indeed encouraged. In addition, remediation studies at point source pollution could also be helpful. A need for a national monitoring program for the organic pollutants including all environmental compartments in Amman-Zarqa area to safeguard or to keep the available resources clean for future generations.

Rückstandanalytik für organische Schadstoffe in Sedimenten aus Amman/Zarqa-Untersuchungsgebietes, Jordanien.

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Zusammenfassung

Ziel dieser Arbeit war die Untersuchung der Konzentration und der saisonalen Verteilungsmuster von Polycyclischen aromatischen Kohlenwasserstoffen (PAH), polychlorierten Biphenylen (PCB) und Chlorbenzolen (CBz) sowie Organochlorpestiziden (OCP) in Sedimenten des Zarqa Flusses in Jordanien. Für die umweltanalytischen Untersuchungen und Monitoringstudien wurden entlang des Zarqa Flusses und seiner beiden Hauptzuflüsse Seil Zarqa und Wadi Dhuliel von Dezember 2000 bis Januar 2002 Sedimentproben entnommen. Im Rahmen dieser Arbeit wurde eine effiziente Extraktions- und Aufreinigungsmethode für eine große Bandbreite von hydrophoben organischen Schadstoffen entwickelt und optimiert. Nach einer Säulenextraktion wurden die Proben einer anspruchsvollen, mehrstufigen Aufreinigung unterzogen, welche neben der Gelpermeationschromatographie (GPC) auch die Säulenaufreinigung an Aluminiumoxid beinhaltete. Nach einem weiteren Aufreinigungsschritt an einer Silicagel-Säule wurde der Extrakt in 2 Fraktionen aufgeteilt. Die erste Fraktion, welche die Biphenyle, die Chlorbenzole und die Organochlorpestizide enthielt, wurden mittels Gaschromatographisch Elektroneneinfangdetektor (GC/ECD) identifiziert und quantifiziert. Für die Analyse der Polycyclischen aromatischen Kohlenwasserstoffe hingegen wurde die gekoppelte Gaschromatographie/Massenspektrometrie (GC/MS) verwendet.

Die adaptierte Analysenarbeit ermöglichte die Quantifizierung der untersuchten Umweltchemikalien im Sediment in Konzentrationen kleiner 0,12 µg/kg für PCB, 0.07 µg/kg für CBz, 0,98 µg/kg für OCP und 1,0 µg/kg für PAH, jeweils bezogen auf die Trockenmasse Sediment. Zur Qualitätssicherung wurden Zusatzversuche durchgeführt, so daß es möglich war, Aussagen über die Nachweis- und Bestimmungsgrenzen zu treffen. Des weiteren wurden der Einfluss der Probelagerung auf die Bestimmung des in den Sedimenten enthaltenen Konzentrationen untersucht.

Die Sedimentprobenahme erfolgte zum einen in einer Sommerperiode (November, 2001) sowie zum anderen im Winter (Januar, 2002). Dabei zeigten sich jahreszeitliche und die niederschlagsbedingte Einflüsse der Schadstoffkonzentrationen. So lagen die Konzentrationen der PAH im Sommer um den Faktor 2 bis 3 höher als in den Wintermonaten. Die Gesamtkonzentrationen der 16 EPA-PAH lagen im Sommer in einem Bereich von 69 bis 3.414 µg/kg und im Winter zwischen 111 und 1.419 µg/kg. Die PAK-Verteilung in den Sedimentproben war des weiteren abhängig von der Struktur sowie dem Molekulargewicht der einzelnen Substanzen. Aufgrund ihrer höheren Persistenz dominierten im Sommer und flussabwärts die 4 und 6 Ring-Aromaten gegenüber den 2-3 Ring-Aromaten. Im Winter und in der Nähe der Quellgebiete wurden die höchsten Konzentration für die 2-3 Ring-Aromaten gefunden. Die Konzentrationsverläufe für die PCB waren denen der PAH ähnlich. Für die 6 Ballschmiter-PCB konnten Gehalte zwischen 1,72 und 9,69 µg/kg gefunden worden. Weiterhin korrelierten die Konzentrationen der PAH und PCB mit den Gehalten an organischen Bestandteilen im Sediment. Die Chlorbenzole konnten nur in sehr geringen Mengen nachgewiesen werden. Hauptsächlich wurden Hexachlorbenzol (HCBz) und in etwas geringeren Konzentration Pentachlorbenzol (PCBz) gefunden. Aufgrund der Untersuchung konnte eine Kontamination des Gebiets mit Rückständen von OCP festgestellt werden. Vorherrschend waren in diesem Fall Metabolite von DDT. Ebenso wie die PAH und PCB könnten die CBz- und OCP-Konzentrationen im Sediment mit den organischen Matrix-Gehalten korreliert werden. Eine Korrelation zwischen nachgewiesener Substanzkonzentrationen und Sedimentpartikelgröße war nur eingeschränkt möglich.

Die vorliegende Arbeit ist eine vorläufige Bestandsaufnahme der Umweltqualität des aquatischen Systems des Zarqa Flusses, um die Kontamination des Sediments mit organischen Schadstoffen zu beschreiben. Der Eintrag von organischen Bestandteilen durch häusliche und industrielle Abwässer führt im Zarqa Fluss zu umweltrelevanten Konzentrationen im Flusssediment. Aufgrund der Ergebnisse dieser Arbeit scheint die Untersuchung des Verhaltens und der Verbreitung von Xenobiotika im Grund- und Oberflächenwasser, im Boden und der darauf angebauten Pflanzen entlang des Zarqa-Flusses dringend notwendig. Um für die zukünftigen Generationen die Umwelt zu schützen und die natürlichen Ressourcen zu bewahren, ist ein nationales Monitorig-Untersuchungs-Programm erforderlich.

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APPENDIX

Table 1. Concentrations of 16 PAH [µg/kg d.w.] using GC/MS for summer season.

Site	NAP	ACY	ACE	FLE	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	ΣPAH
Seil Zarqa	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Z1	118	29	21	77	127	29	72	98	19	49	28	11	24	16	6	25	749
Z2	540	79	54	206	632	78	149	229	23	124	67	64	29	29	8	45	2356
Z3	176	76	63	221	611	73	194	269	59	138	81	18	79	62	23	102	2245
Z4	246	107	99	346	930	101	250	384	63	185	95	33	89	67	42	116	3153
Z5	223	108	87	347	988	116	307	435	71	209	117	37	103	80	44	142	3414
Z6	38	19	15	62	189	25	61	94	12	42	16	12	17	8	ND	20	630
Z7	330	13	12	43	147	22	62	82	15	39	21	10	17	10	5	18	846
Z8	12	5	5	13	46	15	27	34	8	17	12	6	8	7	4	10	229
Z9	3	2	ND	9	30	7	21	23	7	15	10	5	7	6	4	9	158
Z10	3	2	ND	2	4	3	8	5	7	14	11	5	7	7	4	11	93
average	**169**	**44**	**36**	**133**	**370**	**47**	**115**	**165**	**28**	**83**	**46**	**20**	**38**	**29**	**14**	**50**	**1387**
Wadi Dhuleil																	
D1	191	47	81	191	401	65	102	213	52	113	56	14	52	58	ND	49	1685
D2	370	78	145	345	839	95	134	297	60	140	64	15	58	63	20	49	2772
BD3	199	58	92	254	616	85	121	288	57	133	62	15	57	9	17	52	2115
D3	29	50	31	92	216	20	54	133	17	65	20	9	18	15	ND	22	791
AD3	174	49	89	226	461	81	128	302	61	142	67	15	62	66	ND	64	1987
FD3	194	36	83	92	296	29	58	40	13	56	13	15	34	ND	ND	19	978
D4	ND	4	3	10	23	7	15	30	7	19	9	5	6	4	ND	8	150
average	**165**	**46**	**75**	**173**	**407**	**55**	**87**	**186**	**38**	**95**	**42**	**13**	**41**	**31**	**ND**	**38**	**1497**
Zarqa River																	
R1	ND	6	7	18	52	11	26	43	8	25	11	6	11	ND	ND	10	234
R2	ND	3	ND	4	9	3	7	11	4	7	5	3	5	4	ND	4	69
R3	ND	4	4	10	20	6	17	31	7	19	10	5	9	8	ND	8	158
average	**ND**	**4**	**4**	**11**	**27**	**7**	**17**	**28**	**6**	**17**	**9**	**5**	**8**	**4**	**ND**	**7**	**154**

*ND : not detected.

Table 2. Concentrations of 16 PAH [µg/kg d.w.] using GC/MS for winter season.

Site	NAP	ACY	ACE	FLE	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	ΣPAH
Seil Zarqa	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
WZ1	1989	368	351	1136	2488	200	145	402	54	138	33	15	ND	ND	ND	ND	7319
WZ2	117	38	43	123	547	43	108	163	16	70	27	14	16	3	2	33	1362
WZ3	513	21	41	62	122	15	51	60	18	28	23	9	6	12	4	18	1002
WZ4	525	30	28	109	350	28	72	115	12	56	24	14	10	14	2	30	1419
WZ5	4	2	3	9	36	4	18	22	4	10	7	2	3	4	ND	8	136
WZ6	5	2	4	11	23	5	18	27	6	16	7	5	6	ND	ND	4	139
WZ7	6	2	4	11	34	4	10	16	3	7	5	1	3	2	ND	3	111
WZ8	80	21	17	73	219	21	59	8	15	39	28	9	20	16	4	28	657
WZ9	89	22	17	78	291	29	82	119	14	51	24	11	15	13	2	25	882
WZ10	11	12	10	47	145	15	40	60	10	26	14	4	7	7	1	12	421
Average*	**150**	**17**	**19**	**58**	**196**	**18**	**51**	**66**	**11**	**34**	**18**	**8**	**10**	**9**	**3**	**18**	**681**
Wadi Dhuleil																	
WD1	7	8	11	23	53	10	12	20	7	11	7	6	7	6	ND	6	194
WD2	13	15	25	70	225	23	28	55	11	27	12	8	9	ND	ND	ND	521
WBD3	14	14	20	64	184	11	ND	26	ND	ND	ND	ND	ND	ND	ND	ND	333
WD3	13	19	27	65	185	23	22	46	10	27	12	7	10	ND	ND	ND	466
WAD3	39	43	43	109	308	333	35	66	13	40	14	9	9	ND	ND	ND	1062
WFD3	28	25	32	90	253	269	30	61	11	33	11	8	8	ND	ND	ND	859
WD4	15	10	11	28	80	12	20	27	9	16	12	8	8	8	5	13	282
average	**18**	**19**	**24**	**64**	**184**	**97**	**21**	**43**	**9**	**22**	**10**	**7**	**7**	**2**	**ND**	**3**	**531**
Zarqa River																	
WR1	5	3	5	15	42	5	12	18	5	9	8	2	5	4	ND	7	145
WR2	5	3	5	16	54	8	26	35	7	16	10	3	5	4	ND	8	205
WR3	11	6	6	26	89	10	34	43	9	19	11	4	7	5	ND	8	288
WR4	3	ND	3	3	13	3	17	16	9	11	11	4	8	5	ND	5	111
average	**6**	**3**	**5**	**15**	**50**	**7**	**22**	**28**	**8**	**14**	**10**	**3**	**6**	**5**	**ND**	**7**	**187**
other sites																	
Ref.site	2	ND	1	1	2	2	3	2	2	2	4	1	2	2	ND	1	28
I.waste	715	125	90	180	235	250	30	65	25	155	20	25	20	ND	ND	ND	1935

Table 3. CBz and PCB concentration [µg/kg d.w.] for summer season, November 2001.

Site	PCBz ±0.02*	HCBz ±0.12	PCB28 ±0.92	PCB52 ±0.29	PCB101 ±0.08	PCB153 ±0.08	PCB138 ±0.08	PCB180 ±0.08	∑PCB ±1.17
Seil Zarqa									
Z1	<DL**	0.25	1.42	0.14	0.07	0.74	0.20	0.48	3.03
Z2	0.13	0.81	1.85	0.16	0.28	1.01	0.74	0.80	4.84
Z3	0.15	1.43	1.71	0.52	0.35	1.25	0.80	0.82	5.45
Z4	0.24	3.34	2.41	0.76	0.79	1.41	1.31	0.95	7.63
Z5	0.14	1.51	1.34	0.12	0.59	1.48	1.27	0.96	5.75
Z6	<DL	0.98	1.24	0.56	0.40	1.08	0.87	0.85	4.99
Z7	<DL	0.44	0.84	0.15	0.23	0.78	0.65	0.52	3.18
Z8	0.13	2.31	0.68	0.86	0.33	0.58	0.94	0.38	3.77
Z9	<DL	0.32	0.55	0.41	0.61	0.72	1.25	0.44	3.98
Z10	<DL	0.31	5.44	0.16	0.41	0.58	1.00	0.32	7.90
average	**1.28**	**1.17**	**1.75**	**0.38**	**0.41**	**0.96**	**0.90**	**0.65**	**5.05**
Wadi Dhuleil									
D1	0.26	1.18	0.89	0.36	0.55	1.08	1.60	0.96	5.43
D2	0.29	1.07	0.31	<DL	0.53	1.26	1.34	0.96	4.39
BD3	0.31	1.05	3.36	2.23	0.41	1.41	1.21	1.08	9.69
D3	0.27	0.35	4.43	<DL	0.12	0.84	0.91	0.57	6.87
AD3	0.47	1.75	4.91	0.10	0.57	1.30	1.35	1.38	9.61
FD3	<DL	0.56	1.24	0.21	0.31	0.93	0.96	0.60	4.25
D4	<DL	0.61	2.99	0.25	0.27	0.70	0.79	0.37	5.37
average	**0.32**	**0.94**	**2.59**	**0.63**	**0.39**	**1.07**	**1.17**	**0.85**	**6.52**
Zarqa River									
R1	<DL	0.34	1.97	0.07	0.22	0.56	0.78	0.34	3.95
R2	0.58	0.13	0.32	0.11	0.15	0.40	0.53	0.22	1.72
R3	0.53	0.61	2.58	0.61	0.17	0.51	0.63	0.54	5.04
average	**0.56**	**0.36**	**1.62**	**0.26**	**0.18**	**0.49**	**0.65**	**0.37**	**3.57**

*SD was determined for n = 4.
**<DL: below detection limit

Table 4. CBz and PCB concentration [µg/kg d.w.] for winter season, January 2002.

Site	PCBz ±0.02*	HCBz ±0.12	PCB28 ±2.04	PCB52 ±0.02	PCB101 ±0.04	PCB153 ±0.08	PCB138 ±0.12	PCB180 ±0.04	∑PCB ±1.92
Seil Zarqa									
WZ1	0.51	1.51	3.88	1.26	0.52	1.29	1.27	0.55	8.77
WZ2	0.18	1.32	0.66	0.42	0.49	0.89	1.28	0.62	4.36
WZ3	<DL	0.24	0.52	0.72	0.37	0.67	1.17	0.36	3.81
WZ4	0.07	0.83	0.19	0.15	0.36	1.00	1.18	0.70	3.58
WZ5	0.11	0.28	0.15	0.07	0.17	0.53	0.63	0.32	1.87
WZ6	<DL	0.19	2.10	0.80	0.25	0.80	0.84	0.47	5.26
WZ7	0.07	0.16	0.36	0.45	0.13	0.67	0.48	0.30	4.39
WZ8	0.12	0.49	1.16	0.25	0.23	0.79	0.74	0.59	3.76
WZ9	0.34	0.65	1.41	0.30	0.05	0.74	0.34	0.61	3.45
WZ10	0.08	0.26	0.93	0.22	0.07	0.61	0.42	0.44	2.69
average	**0.19**	**0.59**	**1.14**	**0.46**	**0.26**	**0.80**	**0.84**	**0.50**	**4.19**
Wadi Dhuleil									
WD1	<DL	0.54	5.53	0.45	0.16	0.67	0.76	0.42	8.00
WD2	<DL	0.73	1.11	0.57	0.31	0.73	1.07	0.41	4.20
WBD3	<DL	0.42	1.42	0.64	0.34	0.90	1.09	0.38	4.77
WD3	0.07	1.23	3.80	0.54	0.79	1.18	1.78	0.54	8.63
WAD3	0.74	0.74	3.48	0.82	0.34	0.61	0.77	0.31	6.33
WFD3	<DL	0.65	5.22	0.27	0.21	0.70	0.78	0.43	7.61
WD4	0.13	0.39	1.78	0.33	0.28	0.72	0.94	0.33	4.38
average	**0.31**	**0.67**	**3.19**	**0.52**	**0.35**	**0.79**	**1.03**	**0.40**	**6.27**
Zarqa River									
WR1	<DL	0.19	0.96	0.25	0.21	0.67	0.64	0.33	3.06
WR2	<DL	0.13	2.29	0.44	0.41	0.82	0.93	0.42	5.31
WR3	0.09	0.23	1.57	0.73	0.28	0.62	0.67	0.32	4.19
WR4	<DL	0.07	0.11	0.31	0.12	0.41	0.56	0.22	1.73
average	**0.09**	**0.16**	**1.23**	**0.43**	**0.26**	**0.63**	**0.70**	**0.32**	**3.57**
Ref.site	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

*SD was determined for n = 3.

Table 5. Concentrations of 12 pesticides [µg/kg d.w.] analyzed using GC-ECD coupled with DB 5 capillary column for summer period (November, 2001).

Analyte	α–HCH	β–HCH	γ–HCH	δ–HCH	Σ–HCH	Heptachlor	cis-h.epoxide	trans-h.epoxide	Dieldrin	ΣCyclodiene	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	Σ–DDTm
Site	µg/kg	µg/kg	µg/kg	µg/kg	**µg/kg**	µg/kg	µg/kg	µg/kg	µg/kg	**µg/kg**	µg/kg	µg/kg	µg/kg	µg/kg	**µg/kg**
Seil Zarqa															
Z1	2.1	1.9	<DL*	<DL	**4.0**	<DL	<DL	<DL	<DL	**<DL**	1.6	<DL	<DL	4.3	**5.9**
Z2	4.6	<DL	1.4	1.2	**7.2**	<DL	<DL	<DL	1.3	**1.3**	<DL	3.1	3.8	7.4	**14.3**
Z3	7.1	<DL	<DL	1.1	**8.2**	<DL	<DL	<DL	3.8	**3.8**	9.9	9.2	4.9	10.4	**34.4**
Z4	8.0	<DL	<DL	<DL	**8.0**	<DL	4.8	2.0	<DL	**6.8**	14.3	5.8	5.2	12.4	**37.7**
Z5	5.8	<DL	<DL	<DL	**5.8**	<DL	4.3	<DL	9.0	**13.3**	11.2	8.5	6.3	14.4	**40.4**
Z6	2.8	<DL	1.1	<DL	**3.9**	<DL	<DL	<DL	1.4	**1.4**	1.5	4.3	5.3	9.3	**20.4**
Z7	7.4	3.0	1.1	<DL	**11.5**	<DL	<DL	<DL	<DL	**<DL**	<DL	4.1	3.1	7.3	**14.4**
Z8	1.5	1.7	<DL	<DL	**3.2**	<DL	1.9	<DL	<DL	**1.9**	<DL	3.9	2.0	4.5	**10.4**
Z9	2.0	2.0	<DL	<DL	**4.0**	2.0	<DL	<DL	1.6	**3.6**	<DL	<DL	<DL	5.0	**5.0**
Z10	1.4	1.8	<DL	<DL	**3.2**	2.2	<DL	<DL	<DL	**2.2**	<DL	<DL	<DL	3.6	**3.6**
average	**4.3**	**2.1**	**1.2**	**1.2**	**5.9**	**2.1**	**3.7**	**2.0**	**3.4**	**4.3**	**7.7**	**5.6**	**4.4**	**7.9**	**18.7**
Wadi Dhuleil															
D1	1.3	<DL	<DL	3.0	**4.3**	<DL	<DL	<DL	9.7	**9.7**	4.8	10.6	14.6	41.1	**71.1**
D2	3.4	<DL	5.1	<DL	**8.6**	<DL	<DL	<DL	32.3	**32.3**	4.5	35.9	17.6	55.3	**113.3**
BD3	2.9	<DL	<DL	<DL	**2.9**	<DL	<DL	<DL	69.9	**69.9**	7.5	39.5	19.5	59.3	**125.8**
D3	1.2	<DL	<DL	<DL	**1.2**	<DL	<DL	<DL	3.3	**3.3**	5.2	8.5	12.8	33.8	**60.3**
AD3	2.1	<DL	<DL	2.4	**4.5**	<DL	<DL	9.0	15.2	**24.2**	23.7	23.7	20.3	56.6	**124.3**
FD3	1.2	<DL	<DL	<DL	**1.2**	<DL	<DL	<DL	84.5	**84.5**	<DL	10.6	18.5	29.4	**58.4**
D4	<DL	<DL	<DL	1.2	**1.2**	<DL	<DL	<DL	6.7	**6.7**	<DL	<DL	4.6	10.2	**14.8**
average	**2.0**	**<DL**	**5.1**	**2.2**	**3.5**	<DL	**<DL**	**9.0**	**31.7**	**32.9**	**9.14**	**21.5**	**15.4**	**40.8**	**81.2**
Zarqa River															
R1	0.8	<DL	<DL	<DL	**0.8**	<DL	<DL	<DL	1.7	**1.7**	1.4	4.0	3.2	10.9	**19.5**
R2	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	19.1	**19.1**	<DL	3.5	1.9	2.9	**8.3**
R3	0.8	1.4	1.3	<DL	**3.5**	<DL	<DL	<DL	<DL	**<DL**	<DL	3.7	3.0	5.2	**11.9**
average	**0.8**	**1.4**	**1.3**	**<DL**	**2.2**	**<DL**	**<DL**	**<DL**	**10.4**	**10.4**	**1.4**	**3.7**	**2.7**	**6.3**	**13.2**

*<DL :- below detection limit.

Table 6. Concentrations of 12 pesticides [µg/kg d.w.] analyzed using GC-ECD coupled with DB 5 capillary column for winter period (January, 2002).

Analyte / Site	α–HCH µg/kg	β–HCH µg/kg	γ–HCH µg/kg	δ–HCH µg/kg	Σ–HCH µg/kg	Heptachlor µg/kg	cis-h.epoxide µg/kg	trans-h.epoxide µg/kg	Dieldrin µg/kg	ΣCyclodiene µg/kg	o,p´-DDE µg/kg	p,p´-DDE µg/kg	o,p´-DDD µg/kg	p,p´-DDD µg/kg	Σ–DDTm µg/kg
Seil Zarqa															
WZ1	10.1	3.3	2.6	<DL	**16.0**	3.8	<DL	<DL	9.6	**13.4**	<DL	8.7	<DL	4.4	**13.1**
WZ2	4.5	<DL	<DL	<DL	**4.5**	<DL	<DL	<DL	<DL	**<DL**	4.9	3.5	3.7	6.1	**18.3**
WZ3	2.5	1.1	<DL	<DL	**3.6**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	2.1	4.0	**6.1**
WZ4	1.2	2.0	<DL	<DL	**3.2**	<DL	<DL	<DL	<DL	**<DL**	12.1	7.1	4.7	9.7	**33.6**
WZ5	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	2.4	2.7	**5.1**
WZ6	<DL	1.3	<DL	<DL	**1.3**	<DL	<DL	<DL	<DL	**<DL**	4.7	5.2	3.3	5.6	**18.7**
WZ7	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	2.1	<DL	**2.1**
WZ8	<DL	1.2	<DL	1.1	**2.3**	<DL	<DL	<DL	<DL	**<DL**	2.6	21.3	2.6	3.3	**29.8**
WZ9	2.3	2.7	<DL	<DL	**5.0**	<DL	<DL	<DL	<DL	**<DL**	1.4	5.2	3.5	6.8	**16.9**
WZ10	0.8	1.5	<DL	<DL	**2.3**	<DL	<DL	<DL	<DL	**<DL**	<DL	4.3	2.4	5.8	**12.5**
average	**3.6**	**1.9**	**2.6**	**1.1**	**4.8**	**3.8**	**<DL**	**<DL**	**9.6**	**13.4**	**5.14**	**7.9**	**3.0**	**5.4**	**15.6**
Wadi Dhuleil															
WD1	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	2.2	2.6	**4.8**
WD2	<DL	1.0	<DL	<DL	**1.0**	<DL	<DL	<DL	<DL	**<DL**	3.9	3.2	3.6	5.7	**16.4**
WBD3	0.9	1.4	<DL	<DL	**2.3**	<DL	<DL	<DL	<DL	**<DL**	<DL	2.8	3.6	6.0	**12.4**
WD3	3.4	<DL	<DL	<DL	**3.4**	<DL	<DL	<DL	<DL	**<DL**	8.2	8.1	8.9	21.2	**46.4**
WAD3	1.4	1.9	<DL	<DL	**3.3**	<DL	<DL	<DL	<DL	**<DL**	4.9	4.9	5.3	12.8	**27.8**
WFD3	0.9	<DL	<DL	1.2	**2.1**	<DL	<DL	<DL	1.8	**1.8**	5.7	4.0	5.0	7.8	**22.4**
WD4	<DL	<DL	<DL	<DL	**<DL**	<DL	1.4	1.9	<DL	**3.3**	2.4	3.1	3.0	3.0	**11.6**
average	**1.7**	**1.4**	**<DL**	**1.2**	**2.4**	**<DL**	**1.4**	**1.9**	**1.8**	**2.6**	**5.0**	**4.4**	**4.5**	**8.4**	**20.4**
Zarqa River															
WR1	1.4	<DL	<DL	<DL	**1.4**	<DL	<DL	<DL	<DL	**<DL**	<DL	3.2	2.6	2.9	**8.7**
WR2	0.8	1.1	<DL	<DL	**1.9**	1.5	<DL	<DL	<DL	**1.5**	<DL	3.9	3.2	4.0	**11.1**
WR3	0.8	<DL	<DL	<DL	**0.8**	1.7	<DL	<DL	<DL	**1.7**	<DL	3.1	2.7	2.6	**8.4**
WR4	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**
average	**1.0**	**1.1**	**<DL**	**<DL**	**2.1**	**1.6**	**<DL**	**<DL**	**<DL**	**1.6**	**<DL**	**3.4**	**2.8**	**3.2**	**9.4**
I.waste	<DL	<DL	39.8	33.1	**72.9**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**
Ref.site	0.7	1.0	<DL	1.4	**3.1**	<DL	<DL	<DL	<DL	**<DL**	<DL	<DL	<DL	<DL	**<DL**

Table 7. Quality assurance of the analytical procedure for 16 PAH for summer season sampling campaign using GC/MS coupled with DB-5 MS capillary column (30 m), number of replicates was five (n = 5).

Analyte	NAP	ACY	ACE	FLE	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	ΣPAH
Trail	µg/kg*	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Z4T1	402	101	89	318	845	96	229	349	59	167	88	30	81	62	47	104	3067
Z4T2	205	111	111	361	972	105	266	407	65	188	100	33	88	68	42	116	3238
Z4T3	147	106	101	354	990	103	269	408	64	193	101	36	95	70	43	126	3206
Z4T4	249	111	103	386	1029	110	267	426	69	215	102	34	98	69	41	126	3435
Z4T5	227	104	91	310	814	89	221	327	59	163	84	34	82	65	39	106	2815
AVE	246	107	99	346	930	101	250	383	63	185	95	33	89	67	42	116	3152
SD	85	4	8	28	85	7	21	38	4	19	7	2	7	3	3	9	206
RSD	**34.6**	**3.7**	**8.2**	**8.1**	**9.1**	**7.3**	**8.4**	**10.0**	**6.0**	**10.2**	**7.9**	**5.9**	**7.7**	**4.4**	**6.3**	**8.1**	**6.5**

Table 8. Quality assurance of the analytical procedure for 16 PAH for winter season sampling campaign using GC/MS coupled with DB-5 MS capillary column (30 m), number of replicates was three (n = 3).

Analyte	NAP	ACY	ACE	FLE	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	ΣPAH
Trail	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
WFD3T1	28	25	33	86	251	269	29	62	11	33	11	8	8	ND	ND	ND	854
WFD3T2	27	25	32	94	264	278	31	62	12	35	12	9	9	ND	ND	ND	890
WFD3T3	28	24	32	90	243	259	29	59	11	31	10	8	7	ND	ND	ND	831
AVE	28	25	32	90	253	269	30	61	11	33	11	8	8	ND	ND	ND	858
SD	ND**	ND	ND	3	9	8	1	1	ND	2	1	ND	1	ND	ND	ND	24
RSD	**1.7**	**1.9**	**1.5**	**3.6**	**3.4**	**2.9**	**3.2**	**2.3**	**4.2**	**4.9**	**7.4**	**5.7**	**10.2**	-	**-**	**-**	**2.8**

* The results are presented in µg/kg of dry weight sediment sample.
**ND : Not Detected

Table 9. Quality assurance of the analytical procedures for PCBz, HCBz and 6 PCB for summer seasons using GC/ECD coupled with DB-5.

Analyte	PCBz	HCBz	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB180	ΣPCB
Site/Trail	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Z4T1	0.25	NA	2.45	0.76	0.81	1.41	1.30	0.95	7.68
Z4T2	0.18	1.40	1.13	1.10	1.08	1.81	2.18	1.11	8.41
Z4T3	0.20	1.71	1.58	0.79	1.08	1.78	2.21	1.20	8.64
Z4T4	0.21	1.54	2.90	0.48	1.04	1.71	2.11	1.00	9.25
Z4T5	0.17	1.33	0.33	0.33	0.92	1.63	1.97	1.01	6.19
AVE	0.20	1.49	1.68	0.69	0.99	1.67	1.96	1.05	8.03
SUM	1.00	5.98	8.38	3.45	4.94	8.35	9.78	5.27	40.17
SD	0.03	0.15	0.92	0.27	0.11	0.14	0.34	0.09	1.05
RSD	**14.52**	**9.74**	**54.87**	**38.75**	**10.66**	**8.58**	**17.26**	**8.40**	**13.06**

Table 10. Quality assurance of the analytical procedures for PCBz, HCBz and 6 PCB for winter seasons using GC/ECD coupled with DB-5.

Analyte	PCBz	HCBz	PCB 28	PCB 52	PCB 101	PCB 153	PCB 138	PCB180	ΣPCB
Site/Trail	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
WFD3T1	ND	0.65	5.15	0.27	0.21	0.70	0.78	0.43	7.53
WFD3T2	ND	0.42	8.91	0.28	0.24	0.82	0.80	0.36	11.41
WFD3T3	ND	0.33	4.21	0.25	0.34	0.85	1.05	0.43	7.13
AVE	-	0.47	6.09	0.26	0.26	0.79	0.88	0.41	8.69
SUM	-	1.41	18.27	0.79	0.78	2.37	2.63	1.23	26.08
SD	-	0.13	2.03	0.01	0.06	0.07	0.12	0.03	1.93
RSD	-	**28.43**	**33.36**	**4.86**	**22.15**	**8.42**	**14.06**	**8.13**	**22.20**

Table 11. Quality assurance of the analytical procedures for organochlorine pesticides for summer seasons using GC/ECD coupled with DB-5.

Analyte	α-HCH	β-HCH	γ-HCH	δ-HCH	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	Dieldrin	Trans-h.epoxide	Cis-h.epoxide	Heptachlor
Site/Trail	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
Z4T1	6.70	ND	ND	ND	14.41	5.47	5.81	12.56	ND	2.01	5.41	ND
Z4T2	6.04	ND	ND	ND	15.39	6.33	5.05	11.60	ND	1.70	4.19	ND
Z4T3	6.76	ND	ND	ND	8.95	5.91	5.38	12.24	ND	2.32	5.24	ND
Z4T4	7.00	ND	ND	ND	16.82	5.38	4.91	12.56	ND	2.13	4.67	ND
Z4T5	9.03	ND	ND	ND	15.90	5.82	4.74	13.08	ND	1.98	4.60	ND
AVE	7.11	-	-	-	14.29	5.78	5.18	12.41	-	2.03	4.82	-
SD	**1.01**	-	-	-	**2.78**	**0.34**	**0.38**	**0.49**	**--**	**0.20**	**0.44**	-
RSD	**14.25**	**-**	**-**	**-**	**19.47**	**5.89**	**7.29**	**3.92**	**-**	**10.03**	**9.19**	**-**

Table 12. Quality assurance of the analytical procedures for organochlorine pesticides for winter seasons using GC/ECD coupled with DB-5.

Analyte	α-HCH	β-HCH	γ-HCH	δ-HCH	o,p´-DDE	p,p´-DDE	o,p´-DDD	p,p´-DDD	Dieldrin	Trans-h.epoxide	Cis-h.epoxide	Heptachlor
Site/Trail	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
WFD3T1	0.85	0.84	ND	1.91	5.61	3.47	4.68	7.62	1.80	ND	ND	0.38
WFD3T2	1.04	0.66	ND	0.61	5.85	4.50	5.44	7.99	1.64	ND	ND	0.18
WFD3T3	0.81	0.41	ND	1.04	5.54	3.90	4.86	7.70	2.00	ND	ND	0.55
AVE	0.90	0.64	-	1.19	5.67	3.96	4.99	7.77	1.81	-	-	0.37
SD	0.10	0.18	-	0.54	0.13	0.42	0.32	0.16	0.15	-	-	0.15
RSD	**11.10**	**28.10**	**-**	**45.60**	**2.40**	**10.70**	**6.50**	**2.10**	**8.10**	**-**	**-**	**40.50**

Table 13. Confirmation of PCBz, HCBz, and PCB results using GC/ECD coupled to DB-5 (60 m) and DB1701 (45 m) capillary columns for a group of selected samples.

Site	Z4,1		Z5,1		BD3,1		Z10,1		WZ1,1	
capillary column	DB-5	DB1701	DB-5	DB1701	DB-5	DB1701	DB-5	DB1701	DB-5	DB1701
analyte	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
PCBz	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.5	0.2
HCBz	3.3	3.5	1.5	1.7	1.0	0.7	<DL	<DL	1.5	1.3
PCB 28	2.4	1.4	1.3	1.8	3.4	1.8	5.5	9.5	3.9	0.7
PCB 52	0.8	<DL	<DL	<DL	2.2	<DL	<DL	<DL	1.3	<DL
PCB 101	0.8	0.9	0.6	0.7	0.4	0.5	<DL	<DL	0.5	0.7
PCB 153	1.4	1.7	1.5	1.5	1.4	1.8	0.6	0.9	1.3	1.2
PCB 138	1.3	2.0	1.3	1.7	1.2	1.2	1.0	1.4	1.3	1.9
PCB 180	1.0	1.1	1.0	0.9	1.1	0.7	<DL	<DL	0.5	0.6
ΣPCB	7.6	7.1	5.6	6.6	9.7	5.9	7.0	11.8	8.8	5.1

continued....

Site	WZ6,1		WAD3,1		WD3,1		D3,2	
capillary column	DB-5	DB1701	DB-5	DB1701	DB-5	DB1701	DB-5	DB1701
analyte	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
PCBz	<DL	<DL	0.8	5.2	<DL	<DL	<DL	<DL
HCBz	<DL	<DL	0.7	0.6	1.2	7.0	<DL	<DL
PCB 28	2.1	6.4	3.5	5.0	3.8	4.8	4.5	7.0
PCB 52	0.8	<DL	0.8	<DL	0.5	0.4	<DL	<DL
PCB 101	<DL	<DL	<DL	<DL	0.8	1.1	0.1	0.1
PCB 153	0.8	0.8	0.6	0.7	1.2	1.6	0.8	0.6
PCB 138	0.8	1.1	0.8	0.8	1.8	2.5	0.9	0.9
PCB 180	0.5	0.5	<DL	<DL	0.5	0.6	0.6	0.4
ΣPCB	5.0	8.8	5.8	6.5	8.6	11.1	6.9	9.0

*DL:-Detection limits for PCBz, HCBz and 6 PCB are listed in table (3.2).

Table 14. Confirmation of organochlorine pesticides results using GC/ECD coupled to DB-5 (60 m) and DB1701 (45 m) capillary columns for a group of selected samples.

analyte	α-HCH		β-HCH		γ-HCH		δ-HCH		Σ-HCH		o,p´-DDE		p,p´-DDE		o,p´-DDD		p,p´-DDD	
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
column	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701
Site																		
Z3	7.1	6.4	<DL*	<DL	<DL	<DL	1.1	2.0	8.2	8.5	9.9	1.2	9.2	4.7	4.9	2.1	10.4	8.4
Z5	5.8	10.3	<DL	<DL	<DL	<DL	<DL	2.6	5.8	12.9	11.2	1.1	8.5	7.0	6.3	2.5	14.4	10.7
Z8	1.5	1.9	1.7	<DL	0.8	1.0	0.6	<DL	4.6	3.0	0.2	0.3	3.9	4.0	2.0	1.0	4.5	5.8
D1	1.3	3.9	<DL	<DL	<DL	<DL	3.0	3.4	4.3	7.3	4.8	1.9	10.6	6.8	14.6	8.3	41.1	24.9
WZ4	1.2	1.6	2.0	<DL	<DL	<DL	<DL	<DL	3.2	1.6	12.1	8.6	7.1	6.9	4.7	2.6	9.7	11.2
WBD3	0.9	1.0	1.4	<DL	0.4	<DL	0.5	<DL	3.2	1.0	<DL	0.3	2.8	2.7	3.6	2.6	6.0	9.7
R2	0.3	1.1	0.4	<DL	0.3	<DL	0.7	0.9	1.7	2.0	<DL	<DL	3.5	1.4	1.9	0.6	2.9	2.2

continued...

analyte	Σ-DDTm		Heptachlor		cis-h.epoxide		trans-h.epoxide		Dieldrin		Σ-Cyclodiene	
	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg	µg/kg
column	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701	DB 5	DB1701
Site												
Z3	34.4	16.4	<DL	<DL	<DL	3.5	<DL	<DL	3.8	2.3	3.8	5.8
Z5	40.4	21.4	<DL	<DL	4.3	4.5	<DL	<DL	9.0	4.0	13.3	8.5
Z8	10.6	11.2	<DL	<DL	1.9	1.0	<DL	1.1	0.9	1.5	2.8	3.6
D1	71.1	41.8	<DL	<DL	<DL	1.3	<DL	<DL	9.7	2.8	9.7	4.1
WZ4	33.6	29.3	<DL	<DL	<DL	0.6	<DL	<DL	<DL	<DL	<DL	0.6
WBD3	12.4	15.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

*DL:-Detection limits for organochlorine pesticides are listed in **table 3.3**.

Table 15. Sampling dates and site characteristics for summer season.

Site	Sampling site characteristics	Date
Z1	The first sampling site at Seil Zarqa, it is located after the cement cannel and about 5 km northeast Ras Alýn spring	22.11.01
Z2	1 km after the first sampling site. No new water sources into the river	22.11.01
Z3	Domestic and industrial wastewater effluents	22.11.01
Z4	Heavy industrial activities at Arrusseifa area	22.11.01
Z5	Heavy industrial activities at Arrusseifa area	22.11.01
Z6	Domestic and industrial wastewater effluents at Zarqa governrate	22.11.01
Z7	Domestic and industrial wastewater effluents at Zarqa governerate	22.11.01
Z8	Heavy industrial effluents at Zarqa governrate	22.11.01
Z9	About 3 km from Z8, agricultural and traffic activities at Assukhana area	22.11.01
Z10	At the joint point of Seil Zarqa and Wadi Dhuleil tributaries	22.11.01
D1	First site at Wadi Dhuleil, after about 3 km from the outlet of As-Samra WSPs	26.11.01
D2	1 km from D1. Industrial, traffic and agricultural activities	26.11.01
BD3	2 km from Z2 and 20 m before the paper mill	26.11.01
D3	Nearby industrial effluents from paper mill	26.11.01
AD3	20 m after paper mill waste effluents	26.11.01
FD3	800-900 m after paper mill waste effluents	26.11.01
D4	At the joint point of Seil Zarqa and Wadi Dhuleil tributaries	22.11.01
R1	500 m after the joint point of Seil Zarqa and Wadi Dhuleil tributaries	22.11.01
R2	5 km down stream after R1	26.11.01
R3	5 km down stream after R2	26.11.01

Table 16. Sampling dates and site characteristics for winter season.

Site	Sampling site characteristics	Date
WZ1	The first sampling site at Seil Zarqa. It receives wash out water from whole Amman City	26.0102
WZ2	1 km after the first sampling site. No new water sources into the river	26.0102
WZ3	Domestic and industrial wastewater effluents	26.0102
WZ4	Heavy industrial activities at Arrusseifa area	26.0102
WZ5	Heavy industrial activities at Arrusseifa area	26.0102
WZ6	Domestic and industrial wastewater effluents at Zarqa governrate	26.0102
WZ7	Domestic and industrial wastewater effluents at Zarqa governerate	26.0102
WZ8	Heavy industrial effluents at Zarqa governrate	26.0102
WZ9	About 3 km from Z8, agricultural and traffic activities at Assukhana area	26.0102
WZ10	Before the joint point of Seil Zarqa and Wadi Dhuleil tributaries	27.0102
WD1	First site at Wadi Dhuleil, after about 3 km from the outlet of As-Samra WSPs	27.0102
WD2	1 km from D1. Industrial, traffic and agricultural activities	27.0102
WBD3	2 km from Z2 and 20 m before the paper mill	27.0102
WD3	Nearby industrial effluents from paper mill	27.0102
WAD3	20 m after paper mill waste effluents	27.0102
WFD3	800-900 m after paper mill waste effluents	27.0102
WD4	At the joint point of Seil Zarqa and Wadi Dhuleil tributaries	27.0102
WR1	500 m after the joint point of Seil Zarqa and Wadi Dhuleil tributaries	27.0102
WR2	5 km down stream after R1	26.0102
WR3	5 km down stream after R2	26.0102
WR4	10 km down stream after R3	15.0102
Ref.site	Reference site located 120 km south of Amman city and far from anthropogenic activities	29.0102
I. waste (at D3)	Industrial waste effluents from the paper mill	27.0102

Table 17. Some physical sediments properties, sampling period 22-26/11/2001 (Summer season).

Site	Sediment fraction analysis				pH*	TOC [%]	H_2O [%]	Date of sampling
	Clay [%]	Silt [%]	Sand [%]	Texture				
Z1	22.47	7.15	70.38	Sandy clay loam	7.46	2.45	18.65	22.11.01
Z2	23.68	20.45	55.87	Sandy clay loam	7.12	8.41	26.38	22.11.01
Z3	32.54	19.40	48.06	Sandy clay loam	7.04	7.31	26.63	22.11.01
Z4	-	-	-	n.a**	6.69	11.34	30.42	22.11.01
Z5	25.76	26.35	47.89	Sandy clay loam	6.74	10.95	33.95	22.11.01
Z6	17.91	22.25	59.84	Sandy loam	6.90	5.37	28.63	22.11.01
Z7	48.23	27.33	24.44	Sandy clay loam	7.17	5.60	27.98	22.11.01
Z8	15.14	22.97	61.88	Sandy loam	7.54	4.23	25.66	22.11.01
Z9	13.58	26.64	59.78	Sandy loam	7.34	2.41	25.10	22.11.01
Z10	19.47	24.08	56.45	Sandy clay loam	7.59	2.81	22.75	22.11.01
D1	62.56	5.47	31.67	Sandy clay loam	7.17	19.46	61.26	26.11.01
D2	22.55	16.91	60.54	Sandy clay loam	6.36	28.09	52.52	26.11.01
BD3	-	-	-	n.a	6.76	25.58	45.32	26.11.01
D3	8.08	11.19	80.73	Loamy sand	7.11	14.88	43.39	26.11.01
AD3	43.72	9.14	47.14	Sandy clay	6.90	23.69	49.03	26.11.01
FD3	19.88	8.89	71.22	Sandy loam	7.08	17.33	36.92	26.11.01
D4	-	-	-	n.a	7.25	4.34	27.19	22.11.01
R1	11.21	15.48	73.31	Sandy loam	7.12	5.81	26.10	22.11.01
R2	8.52	8.02	83.46	Loamy sand	7.73	1.43	18.00	26.11.01
R3	23.49	17.24	59.27	Sandy clay loam	7.32	5.05	30.31	26.11.01

* pH :- Sediments to water ratio (1:2.5) and shaken for 15 min. before measurement.
** n.a :- not analysed.

Table 18. Some physical sediments properties, sampling period 26-27/01/2002 (Winter season).

Site	Sediment fraction analysis				pH	TOC [%]	H_2O [%]	Date of sampling
	Clay [%]	Silt [%]	Sand [%]	Texture				
WZ1	20.42	6.88	72.70	Sandy clay loam	6.23	13.00	52.46	26.0102
WZ2	22.27	14.55	63.18	Sandy clay loam	7.22	3.84	24.31	26.0102
WZ3	23.91	15.50	60.59	Sandy clay loam	7.07	4.9	29.90	26.0102
WZ4	21.35	14.15	64.50	Sandy clay loam	7.51	2.85	24.12	26.0102
WZ5	16.85	3.52	79.62	Sandy loam	7.95	0.75	20.73	26.0102
WZ6	22.49	16.21	61.30	Sandy clay loam	7.49	7.61	39.92	26.0102
WZ7	10.56	2.77	86.67	Loamy sand	7.57	0.67	21.15	26.0102
WZ8	17.12	8.82	75.06	Sandy loam	7.37	3.83	25.18	26.0102
WZ9	25.88	19.54	54.58	Sandy clay loam	7.33	5.34	23.93	26.0102
WZ10	14.82	6.65	78.53	Sandy loam	7.42	2.26	20.87	27.0102
WD1	19.01	0.51	80.48	Sandy loam	8.14	2.79	23.53	27.0102
WD2	26.56	12.47	60.97	Sandy clay loam	7.56	4.97	39.08	27.0102
WBD3	16.88	13.97	69.15	Sandy loam	7.39	5.96	39.48	27.0102
WD3	50.84	0.67	48.49	Sandy clay	7.28	34.68	70.53	27.0102
WAD3	30.86	0.0	69.14	Sandy clay loam	7.49	17.01	59.68	27.0102
WFD3	18.67	17.10	64.23	Sandy loam	7.18	6.82	49.45	27.0102
WD4	16.99	5.56	77.45	Sandy loam	7.40	3.06	24.62	27.0102
WR1	16.80	6.87	76.33	Sandy loam	7.82	1.82	20.93	27.0102
WR2	19.09	22.15	58.76	Sandy loam-sandy clay loam	7.62	1.96	21.50	26.0102
WR3	16.82	8.56	74.62	Sandy loam	8.01	1.95	23.01	26.0102
WR4	12.76	6.86	80.38	Loamy sand	7.93	1.63		15.0102
Ref.site	20.89	9.58	69.63	Sandy clay loam	8.21	1.89	22.68	29.0102
I. waste (at D3)	-	-	-	-	-	97.49	84.11	27.0102

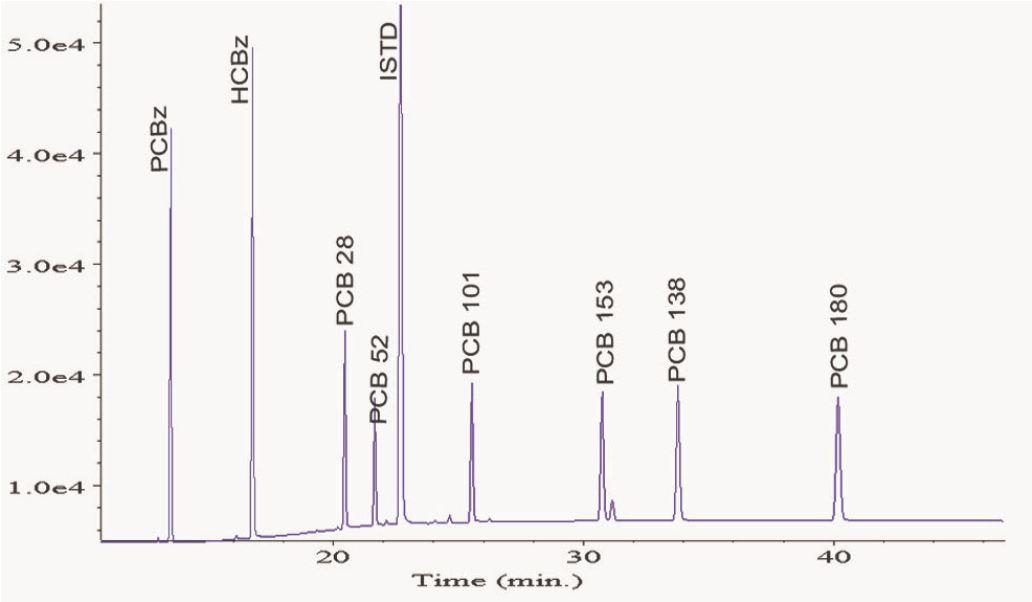

Figure app. 1. GC/ECD chromatogram for standard of PCBz, HCBz and PCB collected using DB-1701 capillary column.

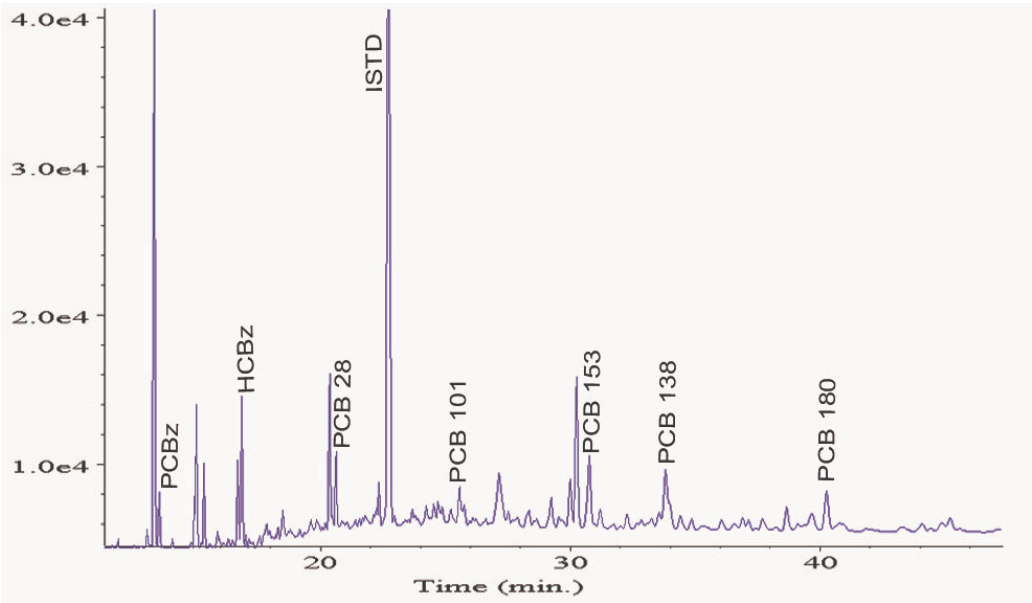

Figure app. 2. GC/ECD chromatogram for sample (BD3) collected using DB-1701 capillary column.

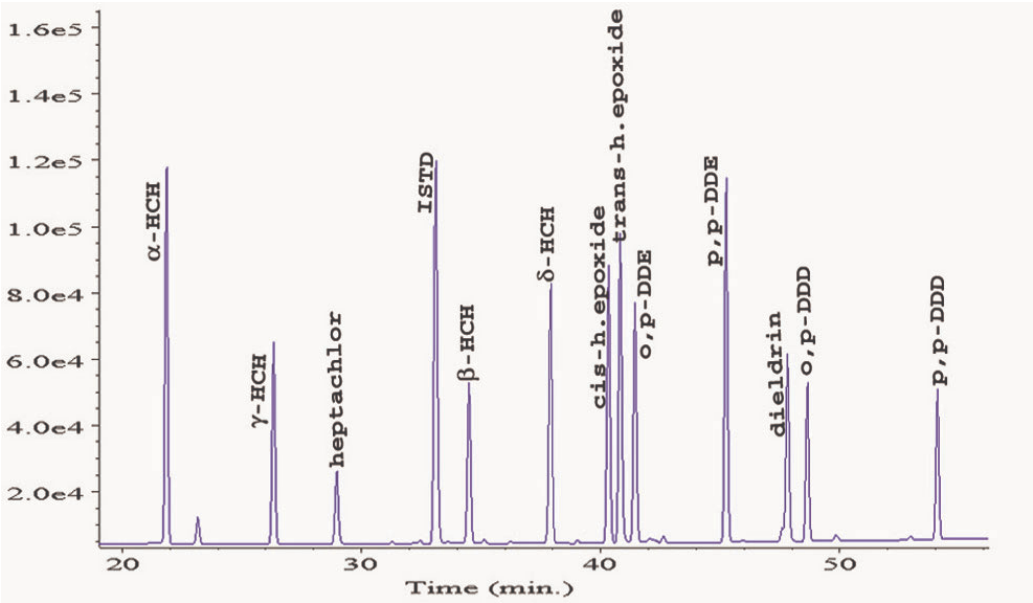

Figure app. 3. GC/ECD chromatogram for standard of organochlorine pesticides (OCP) collected using DB-1701 capillary column.

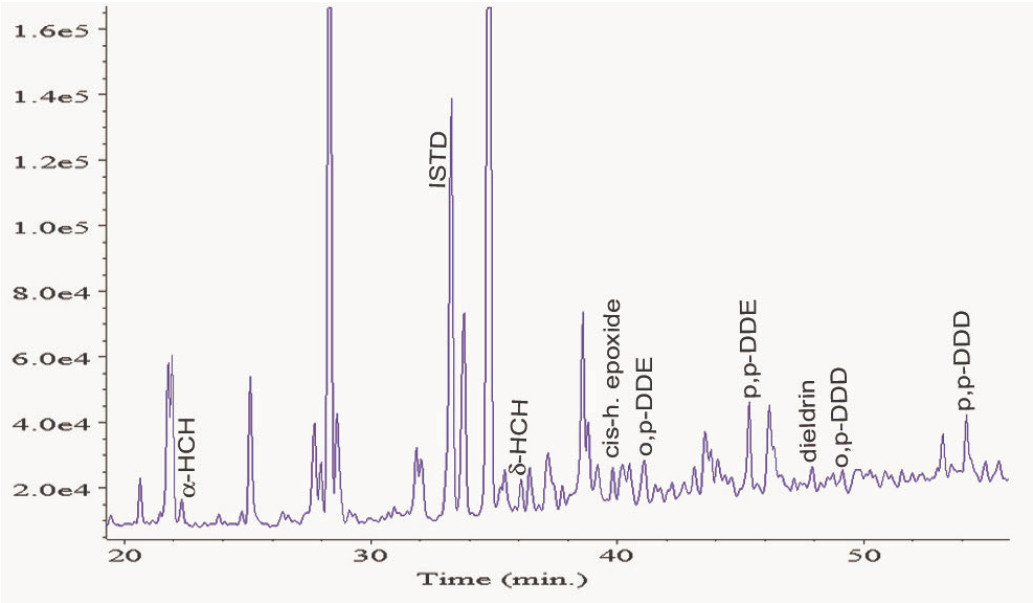

Figure app. 4. GC/ECD chromatogram for organochlorine pesticides (OCP) for sample (Z3) collected using DB-1701 capillary column.

Figure app. 5. Co-effluence of Seil Zarqa and Wadi Dhuliel into Zarqa River.

Figure app. 6.Untreated wastewater leakage along the transport line to As-Samra WSPs.

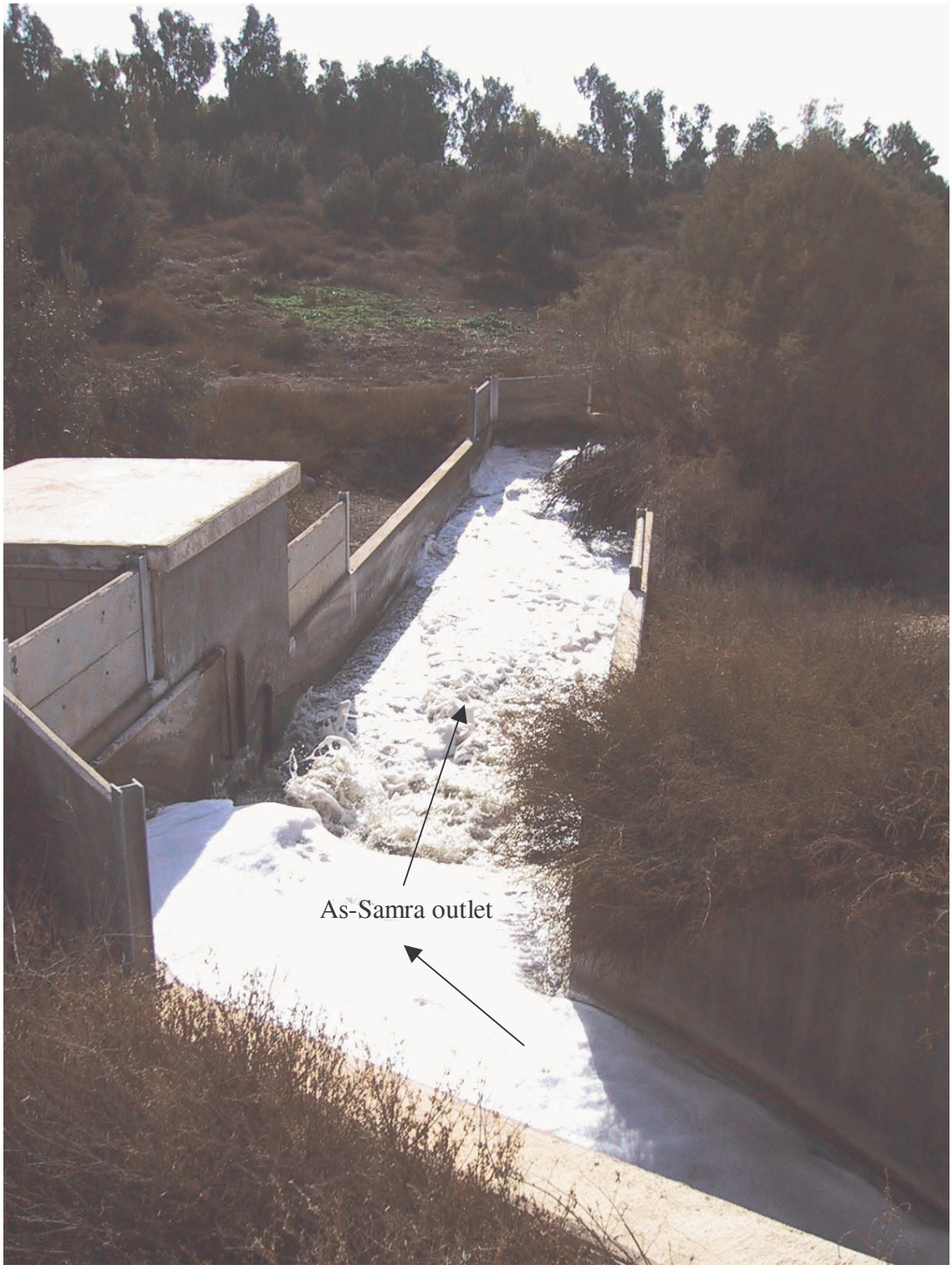

Figure app. 7 . As-Samra outlet into Dhuliel tributary

Figure app. 8. Agricultural activities along Zarqa River banks.

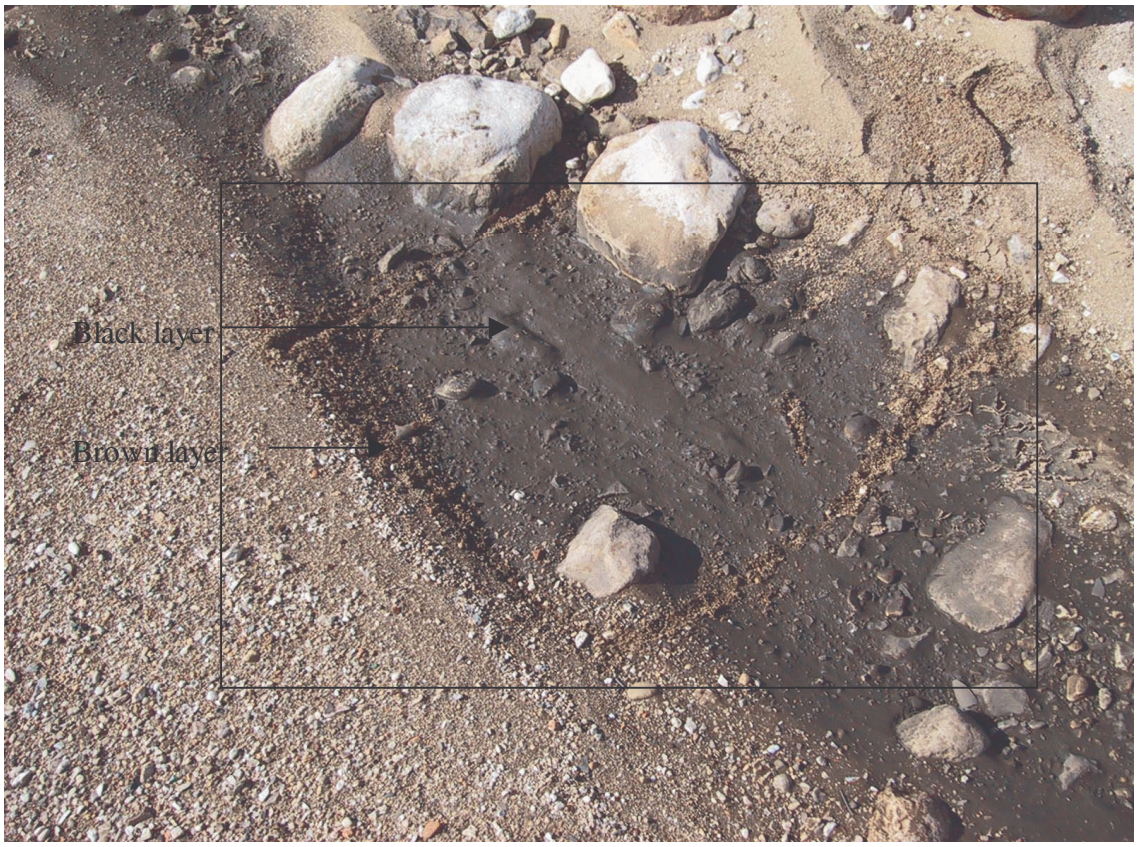

Figure app. 9. Sedimentation profile and sampling technique.

Figure app. 10. Sediment at site.

Lebenslauf

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